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POTENTIAL SOURCES OF ERROR IN GROUND-WATER SAMPLING AT HAZARDOUS WASTE SITES

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INTRODUCTION

The Regional Superfund Ground Water Forum is a group of ground-water scientists representing the U.S. EPA's Regional Superfund Offices that was organized to exchange up-to-date information related to ground-water remediation at Superfund sites. The introduction of error during ground-water sampling is an issue identified by the Forum as a concern of Superfund decision makers.

To address this issue, this paper was prepared under the direction of K. F. Pohlmann of the Desert Research Institute/Water Resources Center, with the support of the Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) and the Superfund Technical Support Project. For further information contact Ken Brown, EMSL-LV Technology Support Center Director, at 702/798-2270 or K. F. Pohlmann at 702/895-0485.

Acquisition of ground-water samples that accurately represent in situ physical, chemical, and biological conditions is critical to all phases of Superfund site investigations. Nonrepresentative data collected during the remedial investigation (RI) may interfere with the characterization of site hydrogeology, contaminant distribution, and the determination of whether ground water is providing a pathway for migration of waste constituents away from the site. The feasibility study (FS) phase of the investigation depends on representative data to adequately define the optimal remediation technologies for the site. Finally, accurate data are required during the remediation phase to determine whether remedial actions are functioning effectively.

Sample error is defined here as the deviation from in situ values of hydrochemical parameters and constituents caused by the conduct of ground-water sampling investigations. Errors in ground-water quality data reduce the ability of samples to accurately represent in situ ground-water conditions resulting in increased variability of analytical results and weakened confidence in ground-water data. As a consequence, the objectives of the site investigation may be jeopardized. To ensure representative data, it is necessary to identify, evaluate, and reduce potential sources of error for every aspect of the sampling program. Errors that are most difficult to identify may be the most critical to sampling programs because important conclusions may be unknowingly based on erroneous or inadequate data.

PURPOSE AND SCOPE

This paper is intended to familiarize RPMs, OSCs, and field personnel with the sources of error inherent to ground-water sampling, and the relative impact of these errors on sample representativeness. Elements of typical sampling protocol will be discussed in relation to how these sources of error can be identified and minimized. Where possible, the error associated with a particular method or material will be quantified and the elements ranked as to their potential for adversely impacting sample representativeness. Some of the elements of sampling protocol to be addressed include monitoring well drilling, design, construction, and purging, sample collection methods and devices, sample filtration, equipment decontamination, sample transport and storage, and analytical methods.

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Each Superfund site has unique geologic, hydrologic, biologic and chemical conditions that may influence the type and magnitude of potential sample errors. This paper provides an overview of sample error; types of error potentially important at each site must be evaluated on an individual basis. Furthermore, while this paper will remain static, the conduct of site investigations will be in a constant state of flux as new technology is developed and as the understanding of contaminant transport and fate and the sampling process is improved. As a result, sources of sampling error described herein may be resolved through the application of new technology and methods while new sources of error are likely to be identified.

MONITORING WELL DESIGN

The design of ground-water monitoring installations must be *consistent with geologic, hydrologic, and hydrochemical conditions* to obtain representative ground-water samples. Important aspects of monitoring well design include length of well intake interval, design of the filter pack and screen, design and installation of borehole seals, and well location.

Intake Length

The length and location of well intakes have important effects on the degree with which samples represent ground-water conditions. Long well intakes (long screens) are open to a large vertical interval and therefore are more likely to provide samples that are a composite of the ground water adjacent to the entire intake. Conversely, short intakes (short screens) may be open *to a single strata or zone of contamination and are more likely to* provide samples that represent specific depth intervals. Wells that are screened over more than one depth interval (multi-screened wells), regardless of their screen lengths, may impact ground-water conditions and samples in much the same way as long-screened wells.

Long-screened wells have been suggested as being more cost effective in detection monitoring than several short-screened wells because they sample greater vertical sections of aquifers (Giddings, 1986). However, pumping-induced vertical flow in wells with long screens can impact ground-water flow and contaminant concentrations near the well (Kaleris, 1989). In addition, when ground-water contamination is vertically stratified, *composite samples collected from a long-screened well* represent some sort of average of concentrations adjacent to the screen, and provide little information about the concentrations in individual strata. In particular, in cases where contaminants may be of low concentration and restricted to thin zones, long-screened wells may lead to dilution of the contaminants to the point where they may be difficult to detect (Cohen and Rabold, 1987). Likewise, long-screen wells intersecting contaminants of differing densities may allow density-driven mixing within the well bore and subsequent dilution of contaminant concentrations (Robin and Gillham, 1987). The use of inflatable packers to isolate specific zones within a long screen may not be an effective solution because ground water may flow vertically through the filter pack from other zones in response to the reduced hydraulic head in the packed-off zone during sampling.

Vertical head gradients in aquifers near long-screened wells may lead to error in two ways: (1) if contaminants are moving through a zone with low hydraulic head, cleaner water moving from zones of higher head may dilute the contaminants, leading to detection of artificially low concentrations, and, (2) if higher concentrations of contaminants are moving through a zone of high hydraulic head, cross-contamination between water-bearing zones may occur via the well bore (McIlvride and Rector, 1988). These workers describe a case history in which two aquifer zones were identified at a site, with only the top zone contaminated with VOCs. Wells screened only in the contaminated zone resulted in detection of VOCs in the few hundred µg/L range while samples collected from long-screened wells open to both intervals showed no VOC contamination. A numerical flow model of a long-screened well developed by Reilly et al. (1989) demonstrated that very low head gradients can lead to substantial cross-flow within long-screened wells. At sites where delineation of vertical hydraulic and concentration gradients is important, errors can be reduced by utilizing a system of *nested short-screened* wells that can more accurately characterize the contaminant distribution.

Multilevel sampling devices provide an alternative monitoring technique in situations where vertical head gradients are important or where contamination is vertically stratified. These devices can be installed in such a way that individual zones can be sampled separately without vertical movement of ground water or contaminants between zones. Using a multilevel device, Smith et al. (1987) detected a zone containing nitrate concentrations over 10 mg/L that had been previously undetected by observation wells with two-foot screens. The samples from the multilevel sampler also detected large vertical gradients in electrical conductivity (EC) and chloride that were not *detected with the monitoring wells.*

Residential and municipal water-supply wells that are often used during early phases of RI programs are generally constructed with long screens, therefore concentrations of contaminants in samples collected from these wells may not represent ambient ground-water concentrations. When defining human receptors this may not be an issue because the overall quality of ground-water extracted from water-supply wells may not reflect the quality of water in individual strata. In these cases, dilution may reduce concentrations of contaminants to within health-based standards. However, gross errors may be introduced into the analysis if these concentrations are used for detailed delineation of the geometry and concentrations of *contaminant plumes or detection of contaminants at very low* concentrations.

To mitigate hazards, waste management options at Superfund sites may include remediation of contaminated ground water by pumping and treatment. Long-screen wells are often the most effective for extraction of ground water because they are hydraulically more efficient than wells with short screens. However, because accurate ground-water contaminant concentrations cannot be determined from these wells it may be necessary to install separate wells for monitoring the progress of ground-water extraction and treatment.

Filter Pack and Well Intake

Suspended solids that originate from drilling activities or are mobilized from the formation during development, purging, or sampling may disrupt hydrochemical equilibrium during sample collection and shipment. A properly designed combination of

filter pack and well intake provides an efficient hydraulic connection to a water-bearing zone and minimizes the suspended solids content of sampled water. However, to be most effective, filter pack and well intake design must be based on the sediments encountered in each borehole. Inadequate well performance resulting from application of a generic well design may lead to incomplete well development and high suspended solids content in samples. Descriptions of the methods of filter pack and intake design can be found in Driscoll (1986) and Aller et al. (1989).

Artificial filter packs should be composed of a chemically-inert material so as to reduce the potential for chemical alteration of ground water near the well. Clean silica (quartz) sand is generally recommended and widely used because it is nonreactive under most ground-water conditions. Other types of materials may induce chemical changes. For example, filter pack materials containing calcium carbonate, either as a primary component or as a contaminant, may raise the pH of water that it contacts and lead to precipitation of dissolved constituents (Aller et al., 1989).

The use of a tremie pipe to install filter pack materials minimizes the potential for introducing sample error to this phase of well construction. Dropping filter pack materials directly into an uncased borehole may lead to cross-contamination by mobilizing sediments or ground water between depth intervals. Furthermore, installation of filter pack materials by methods which introduce water to the borehole may modify hydrochemistry to an unknown extent or add contaminants to the sampling zone. Water-based methods may also lead to cross-contamination within the borehole.

Borehole Seals

Borehole seals, generally composed of expandable bentonite or cement grout, are well-known as potential sources of sampling error. The expandable bentonite clay used in many seals has high ion exchange capacity which may alter major ion composition of water(Gillham et al., 1983) or concentrations of contaminants that form complexes with these ions (Herzog et al., 1991). The effects of these reactions are seldom revealed by measurement of field parameters and normally-conducted analyses, but in cases of extreme sodium bentonite contamination may be seen as abnormally high sodium concentrations.

Cement grout can also significantly influence ground water chemistry, particularly if the grout doesn't set properly. Contamination by grout seals, which generally results from its calcium carbonate content and high alkalinity, may be identified by elevated calcium concentrations, pH (generally over 10 pH units), EC, and alkalinity (Barcelona and Helfrich, 1986). These workers found that cement contamination of several wells persisted for over 18 months after well completion and was not reduced by ten redevelopment efforts. Barcelona et al. (1988a) indicate that solution chemistry and the distribution of chemical species can be impacted by cement contamination although these impacts have not been quantified to date. In low-permeability sediments, the impacts of grout materials may be much greater due to insufficient flushing of the installation by moving ground water.

Contamination from borehole seals can be minimized by separating the seals from sampling zones by fine-grained transition sand, estimating the volume of seal material required before installation to more easily detect bridging problems during emplacement, and by allowing sufficient time for the seals to set. In addition, cement grout can be isolated from sampling zones by installation of a bentonite seal. Error can also be reduced by installing boreholes seals with a tremie pipe. Dropping seal materials directly into an uncased borehole may lead to cross-contamination by mobilizing sediments or ground water between depth intervals, or may contaminate sampling zones if the seal materials are dropped past the sampling zone depth. Furthermore, installation of seal materials by methods which introduce water to the borehole may modify hydrochemistry to an unknown extent or introduce contaminants to the sampling zone. Water-based methods may also lead to cross-contamination within the borehole.

Well Location

The location of monitoring wells with respect to ground-water contaminant plumes is important to the accurate depiction of contaminant movement and concentration distribution, especially in areas where concentration gradients are large. A discussion of optimum well placement is beyond the scope of this document, but aspects of this topic can be found in the works of Keith et al. (1983), Meyer and Brill (1988), Scheibe and Lettenmaier (1989), Spruill and Candela (1990), and Andricevic and Foufoula-Georgiou (1991). These investigators discuss various aspects of monitoring well network design and how monitoring well coverage of the area under investigation relates to accurate quantification of spatial variation in hydrochemical parameters. Generally implied within network design is the reduction in error associated with delineating spatial variation. Sampling from wells whose locations were determined without adequate consideration of network design and geologic, hydraulic, and hydrochemical conditions may lead to significant errors in data interpretation and conclusions. For example, resolution of concentration distribution may be reduced in areas where wells spacing intervals are too large for the scale of the investigation.

To summarize the topic of monitoring well design, collection of accurate ground-water quality data in three dimensions is strongly dependent on the design of the ground-water monitoring system, including both individual wells and well networks. Significant errors can be introduced into sampling data, and the resultant conclusions, if well intakes and filter packs are not designed for ambient conditions, or are placed at inappropriate depths or over excessive vertical intervals, or if borehole seals are improperly installed. Furthermore, the design of monitoring well networks may introduce error by inadequately representing spatial variation through inadequate coverage of the site. Although the magnitude of these errors is heavily dependent on the geologic, hydraulic, and hydrochemical conditions present at a particular site, order of magnitude effects are easily within the realm of possibility.

DRILLING METHODS

Long-term or permanent disturbance of hydrogeologic and hydrochemical conditions may result from the drilling method used for monitoring well installation, possibly leading to significant error during subsequent ground-water sampling. Drilling methods may disturb sediments, allow vertical movement of ground water and/or contaminants, introduce materials foreign

to the subsurface, and clog void spaces. The extent to which conditions are altered depends on the drilling method utilized and the nature of the geologic materials (Gillham, et al., 1983). In addition, the properties of the contaminants at the site will influence their sensitivity to the impacts of drilling.

Monitoring wells are commonly constructed by auger, rotary, drill-through casing, and cable-tool methods. Auger drilling methods utilize hollow- or solid-stem auger flights and are generally restricted to use in unconsolidated materials. Rotary techniques are classified based on the composition of the drilling fluid (water, air, and various additives), the mode of circulation (direct or reverse), and the type of bit (e.g. roller cone, drag, or button) and are adaptable to most geologic conditions. The drill-through casing method utilizes rotary or percussion drilling techniques but uses a casing driver to advance temporary casing in conjunction with the advancing borehole. In cable-tool drilling, the borehole is advanced by alternately raising and lowering a heavy string of drilling tools suspended from a cable. Temporary casing can also be advanced as drilling progresses.

Some drilling methods may alter the hydrogeologic environment by smearing cuttings (particularly fine sediments) vertically along the borehole wall. This action may form a mudcake that can reduce the hydraulic efficiency of the borehole wall and modify ground-water flow into the completed well (McIlvride and Weiss, 1988). Smearing may also transport sediments between zones and alter the vertical distribution of contaminants adsorbed onto these sediments. In addition, methods that mix sediments horizontally near the well bore may affect the transport of contaminants near the completed well (Morin, et al., 1988).

Vertical movement of ground water may occur during drilling, primarily in situations where the borehole remains uncased during drilling operations. Ground water can be transported vertically by circulating drilling fluid or by hydraulic head differences between zones. In situations where contaminated ground water is vertically stratified, vertical ground-water movement may cause cross-contamination within the well-bore and adjacent formation (Gillham et al., 1983). Movement of ground water and contaminants between zones may also disrupt hydrochemical equilibrium near the well.

Drilling activities can alter hydrochemistry as a result of contact with introduced materials foreign to the subsurface environment. For example, lubricants or hydraulic fluids may enter the borehole directly by falling from the drilling rig or may enter indirectly via drilling fluids. In the latter case, contaminants may originate in mud pumps, air compressors, or down-hole drilling equipment. Soils or other material from the drilling site may also enter the open borehole or may adhere to drilling equipment as it is prepared for use. However, the material most commonly introduced to boreholes is drilling fluid, which is used to remove cuttings, stabilize the borehole wall, and provide cooling, lubrication, and cleaning of the bit and drill pipe (Driscoll, 1986). Drilling fluids commonly are composed of water or air alone or in combination with clay (usually bentonite) and/or polymeric additives.

Water from water-based drilling fluids that migrates away from the borehole and mixes with ambient ground water may alter hydrochemical conditions (Aller et al., 1989). For example, introduction of a different water type may add contaminants or disrupt hydrochemical equilibrium and cause precipitation of dissolved constituents. During sampling, some of these precipitates may be redissolved by ground water flowing toward the well causing non-representative samples.

The bentonite additives used in many drilling fluids have a high capacity for ion exchange and may alter hydrochemistry of ground-water samples if not completely removed from the borehole and surrounding formation (Gillham et al., 1983). Ion exchange reactions that alter major ion composition may also affect the concentrations of contaminants that form complexes with these ions (Herzog et al., 1991). Organic polymeric additives can introduce organic carbon into ground water and provide a substrate for microbial activity leading to errors in water quality observations for long periods. Barcelona (1984) reported that total organic carbon (TOC) levels in wells drilled with fluids containing organic additives remained over three times higher than background levels for two years. In that study, TOC levels could not be reduced to less than two times background levels, even after substantial pumping.

The presence of drilling fluids in the formation surrounding well installations, even after well development, was shown by Brobst and Buszka (1986). That study, which used chemical oxygen demand (COD) as an indicator of the presence of drilling fluid, tested three additives of water-based drilling fluids: guar fluid, guar fluid with a breakdown additive, and bentonite. Brobst and Buszka (1986) reported that, using standard well purging and sampling methods, COD levels were elevated for 50 days in a well drilled with the guar-and-additive fluid, 140 days in a well drilled with bentonite, and 320 days in a well drilled with the guar fluid alone. More intense well purging reduced the COD levels, but not to background values.

Contaminants present in drilling fluid may also mix with ground water and bias sampling results. Mud pumps used with water-based drilling fluids can add trace quantities of lubricants to the fluid and deposit them in the wellbore and surrounding formation. Air compressors used to develop and maintain pressure of air-based drilling fluids may have similar impacts. Filtration units in air-based systems are designed to prevent this occurrence, however, if feasible, the air stream should be sampled during drilling to determine the effectiveness of the filter. Filtration is generally not possible for water-based systems so if ground water samples are to be collected for compounds related to these lubricants it may be necessary to sample the drilling fluid before it enters the borehole.

An outline of potential impacts of drilling methods on ground-water sample quality is shown in Table 1, which was compiled from the work of Scalf et al. (1981), Gillham et al. (1983), Keely and Boateng (1987), Aller et al. (1989), and Herzog et al. (1991).

WELL DEVELOPMENT

Ground-water monitoring wells are developed to restore the sampling zone to conditions present prior to drilling so that sampled ground water can flow unimpeded and unaltered into the well. Materials associated with the drilling process, including borehole wall mudcake, smeared and compacted sediments, and drilling and other fluids, all must be removed from the sampling zone to the extent possible. This can be accomplished

TABLE 1. POTENTIAL IMPACTS OF DRILLING METHODS ON GROUND-WATER SAMPLE QUALITY

Method	Potential Impacts
Auger	Drilling fluids generally not used but water or other materials added if heaving sands are encountered may alter hydrochemistry
	Smearing of fine sediments along borehole wall
	Vertical movement of ground water and/or contaminants within borehole
	Lateral mixing of sediments near well bore
Rotary	Drilling fluids are required and may cause cross-contamination, vertical smearing of sediments, alteration of hydrochemistry, and introduction of contaminants
	Smearing of fine sediments along borehole wall
	Vertical movement of ground water and/or contaminants within borehole
Drive-Through-Casing	Drilling fluids required but advancing casing reduces potential for drilling fluid loss, cross-contamination, and vertical smearing of sediments, ground water, and contaminants.
Cable Tool	Advancing casing reduces potential for cross-contamination, and vertical smearing of sediments, ground water, and contaminants.

in monitoring wells by several methods including surging with a surge block mechanism, surging and pumping with compressed air, pumping and overpumping with a pump, jetting with air or water, backwashing with water, and bailing. All of these methods have the potential (to varying degrees) to influence the quality of ground water samples; the extent depends on the nature of their action and the condition of the sampling zone after drilling.

Development should be considered complete when representative samples can be collected and can continue to be collected indefinitely. Unfortunately, under most ground-water sampling circumstances determining when samples are representative of in situ conditions is not possible, so some related criteria are often chosen. Ideally, these criteria should include (1) the production of clear water during development, and (2) the removal of a volume of water at least equal to the amount lost to the formation during drilling and well installation (Kraemer et al., 1991). In addition, certain conditions may require that development be continued after the well has been allowed to recover from the first round of development efforts. This condition may exist if the first round of samples exhibit turbidity.

Incomplete or ineffective well development may allow drilling and other introduced fluids to remain in the sampling zone or may not remove all mudcake or smeared sediments from the borehole wall. The presence of these materials may introduce error by disrupting hydrochemical equilibrium or by introducing contaminants to the well or sampling zone. In addition, these materials can reduce the hydraulic conductivity of the filter pack and formation and modify ground water flow near the well before and during sampling.

Development methods that utilize air pressure can entrap air in the filter pack and formation, disrupt hydrochemical equilibrium through oxidation, or introduce contaminants from the air stream to the formation and filter pack. These effects may be reduced if precautions are taken to eliminate air contact with the well intake. The addition of water during development may modify hydrochemistry to an unknown extent or may introduce contaminants to the sampling zone, even if all the water is removed during development. In light of these potential problems, jetting methods that inject air or water directly above the well intake are not recommended (Keely and Boateng, 1987). Likewise, other methods that introduce air or water to the well (surging and pumping with compressed air, and backwashing, for example) also may not be suitable for monitoring well development (Aller et al., 1989).

Development of wells at very high rates may displace filter pack and formation materials and reduce the effectiveness of the filter pack, particularly if the method involves excessive surging (Keely and Boateng, 1987). On the other hand, development at low rates (as is generally attained with sampling pumps) may not provide enough agitation to meet development objectives (Kraemer et al., 1991). In many monitoring well situations, using surge-block methods to loosen material and either pumping or bailing to remove the material has been found to be an effective development technique (Aller et al., 1989).

In low-yield wells, surging methods may result in excessive mobilization of fine-grained materials. For example, in a study conducted in fine-grained glacial tills, Paul et al. (1988) found that auger-drilled wells developed by surge-block methods produced samples with up to 100 times greater turbidity than samples from similar wells developed by bailer. In addition, the turbidity of samples from the surged wells did not significantly decrease after a second round of sampling while samples from the bailed wells showed a four-fold decrease (Paul et al., 1988). Because these wells were drilled in low permeability sediments without added fluids, the action of drawing down the water level within the well by bailing may have been sufficient to provide adequate development. On the other hand, bailing or pumping techniques alone may not be effective in wells constructed by drilling methods that introduce fluids or cause significant disturbance of sediments because the development force is dissipated by the filter pack.

The potential impacts of monitoring well development on ground-water sample quality are outlined in Table 2 which is

TABLE 2. POTENTIAL IMPACTS OF DEVELOPMENT METHODS ON GROUND-WATER SAMPLE QUALITY

Method	Potential Impacts
Surging with surge block	Displacement of filter pack and formation materials or damage to the well intake (primarily a problem in poorly designed and constructed wells when surging is conducted improperly)
	Excessive mobilization of fine-grained materials from low-permeability formations
Surging and pumping with compressed air	Entrapment of air in filter pack and formation
	Disruption of hydrochemical equilibrium
	Introduction of contaminants
Pumping and over-pumping with pump	Low-volume pumps may be incapable of sufficient surging action (primarily in high-yield wells with little or no drawdown)
Jetting with air or water	Entrapment of air in filter pack and formation
	Disruption of hydrochemical equilibrium
	Introduction of contaminants
	Excessive mobilization of fine-grained materials from low-permeability formations
Backwashing with water	Disruption of hydrochemical equilibrium
	Introduction of contaminants
Bailing	May be incapable of sufficient development action

based on the work of Keely and Boateng (1987), Paul et al. (1988), Aller et al. (1989), and Kraemer et al. (1991).

MATERIALS

Transfer of ground water from the subsurface sampling zone to a sample container at ground surface often involves contact of the sample with a variety of materials comprising the well, sampling device, tubing, and container. Some of these materials have the potential to bias chemical concentrations in samples as a result of sorption, leaching, and chemical attack, and biological activity (Barcelona et al., 1983). As a result, the materials selected for ground-water sampling must be appropriate for the hydrochemical conditions at the site and the constituents being sampled. Other factors that may influence the choice of materials, including costs verses benefits, availability, strength, and ease of handling, can be found in Aller et al. (1989).

Materials commonly used in the ground-water sampling train can be divided into five general categories (modified from Nielsen and Schalla, 1991):

1. fluoropolymers, which include polytetrafluoroethylene (PTFE), tetrafluoroethylene (TFE), and fluorinated ethylene propylene (FEP);
2. thermoplastics, which include polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), polypropylene (PP), and polyethylene (PE);
3. metals, which include stainless steel (SS), carbon steel, and galvanized steel;
4. silicones; and
5. fiberglass-reinforced, which include fiberglass-reinforced epoxy (FRE) and fiberglass-reinforced plastic (FRP);

This document will focus on the most commonly used materials including the rigid materials PTFE, PVC, and metals (particularly SS) and the flexible materials PE, PP, PTFE, PVC, and silicone.

Chemical and Biological Impacts

Sorption, which includes the processes of adsorption and absorption, may remove chemical constituents from samples thereby reducing the concentrations of these constituents from levels present in the ambient ground water. If compounds present in the ground water are removed entirely, false negative analytical results will be produced. Additionally, desorption of compounds previously sorbed can occur if water moving past the material contains lower concentrations of the sorbant than exists in the material. In this case, contaminants may be detected in samples that do not exist in the ground water, causing false positive analytical results. Sorption/desorption processes may be particularly important in situations where contaminant concentrations are at trace levels and change with time or where samples contact potentially sorbing materials for long periods (for example, during water level recovery in low-yield wells or in inadequately purged wells).

Leaching of chemical constituents from some types of materials may occur under the conditions present at many hazardous waste sites. Constituents of the materials' matrix, or compounds added during fabrication, storage, and shipment, may have solubilities in water high enough to be leached under natural ground-water conditions (Gillham et al., 1983). Ground water contaminated by high concentrations of organic solvents may cause significant degradation of the matrix of some polymeric materials, resulting in leaching of various compounds (Barcelona et al., 1983). As a result, false positive analytical results can be produced if the source of target constituents in ground-water samples is leaching from casing materials rather than the ambient ground water. In addition, corrosion of metal casing may introduce dissolved metals to ground-water samples and reduce the integrity of the well.

Under certain ground-water conditions, well-casing materials may impact biologic activity, and vice versa, in the vicinity of the well (Barcelona et al., 1988b) and lead to errors that are difficult to predict. For example, the presence of dissolved iron in ground-water may favor the growth of iron bacteria near metallic wells and degrade the casing and screen (Driscoll,1986). In addition, permeation of contaminants or gases through materi-

als may be a potential source of sample bias with flexible tubing (Barker et al., 1987; Holm, 1988) but is unlikely with rigid materials, as demonstrated by Berens (1985) for organic compounds and rigid PVC pipe over time periods less than 100 years.

Rigid Materials

Rigid materials that contact ground-water samples are generally used in well casings and screens, sampler components, and filtration equipment.

PTFE

PTFE has been widely considered the best choice for monitoring well materials because of its apparent resistance to chemical attack and low sorption and leaching potential. However, several recent laboratory studies have shown that rigid PTFE materials actually demonstrate a significant ability to sorb hydrocarbons from solution. Sykes et al. (1986) found that PTFE materials sorbed several hydrocarbons from a solution containing concentrations of approximately 100 µg/L, but did not report quantities. Parker et al. (1990) found that rigid PTFE materials sorbed significant quantities of all tested chlorinated organics and a nitroaromatic; higher, in fact, than PVC materials. These workers found that losses of some of these compounds from test solutions (initial concentrations of each compound were approximately 2 mg/L) exceeded 10% within eight hours. Likewise, rigid PTFE materials showed significant sorption of aromatic hydrocarbons in 24 hours of exposure for benzene, and six hours for several other hydrocarbons (Gillham and O'Hannesin, 1990). After eight weeks of PTFE exposure to benzene, 75% losses from the test solution were observed.

In contrast, PTFE materials tend to show lower potential for interaction with trace metals than PVC or SS (Barcelona and Helfrich, 1986). For example, lead was the only metal of four tested (arsenic, chromium, cadmium, and lead) in a laboratory study to be actively sorbed onto PTFE materials although only 5% of the lead concentration in the test solution was removed after 24 hours of exposure (Parker et al., 1990).

PVC

Early studies of PVC materials found substantial potential for sample error from sorption and leaching effects. Many of the conclusions about sorption were based on flexible PVC, which has a much higher sorption potential than rigid PVC. Leaching of high VOC concentrations was found to be a particular problem from PVC solvents and cements used for casing joints and bailer construction. Boettner et al. (1981) found cyclohexanone, methylethylketone, and tetrahydrofuran leached into water at concentrations ranging from 10 µg/L to 10 mg/L for more than 14 days after the glue was applied to PVC pipe. In addition to these compounds, methylisobutylketone was detected in ground-water samples several months after the installation of cemented PVC casing (Sosebee et al. (1982). The results of these studies indicate that alternative methods of joining PVC casing, such as threaded joints, should be utilized to reduce sample error.

Laboratory investigations show that threaded PVC well materials sorb hydrocarbon compounds, but often at lower rates than other polymers, including PTFE. Miller (1982) found little absorption of six VOCs over a six-week period, with the exception of tetrachlorethylene which showed a 50% decline in concentration in solution. These sorption results were significantly lower than those from PE and PP casing materials. Subsequent leaching from PVC was found to be at insignificant levels for all six VOCs. Gillham and O'Hannesin (1990) found that significant sorption onto rigid PVC from a solution containing six hydrocarbons did not occur until 12 hours after exposure. The PVC results were in contrast to three other rigid polymers (PTFE, FEP, and polyvinylfloride) that showed significant uptake of at least one of the six compounds within three hours of exposure. After eight weeks of PVC exposure to benzene, 25% losses were observed from the original solution concentration of approximately 1.2 mg/L. Similar results were reported by Parker et al. (1990) who found that PVC sorption of 10% of initial organic compound concentrations didn't occur until over 72 hours of exposure, while PTFE sorption of 10% of three of the 10 tested organics occurred within eight hours of exposure. Two dichlorobenzene isomers showed the highest sorption rates on PVC: significant losses were observed within eight hours. Sykes et al. (1986) found no significant differences between PVC, PTFE, and SS materials in their tendency to sorb six organics at concentrations of approximately 100 µg/L each.

The results of these research studies indicate that rigid PVC materials have relatively low potential for sorption and leaching of organic compounds relative to other polymers when exposed to dissolved concentrations generally found at hazardous waste sites. However, Berens (1985) demonstrated that PVC may soften and allow permeation of organic compounds if exposed to nearly undiluted solvents or swelling agents for PVC. For this reason, PVC well casing should be avoided under these conditions.

PVC materials may also react with some trace metals. Miller (1982) concluded that in a six-week exposure to test solution, PVC materials did not affect chromium concentrations but that lead concentrations declined over 75%. A subsequent experiment showed that over 75% of the initial lead concentrations were desorbed from the PVC material. Parker et al. (1990) found that rigid PVC showed no measurable sorption or leaching of arsenic or chromium but that cadmium was leached and lead sorbed. For example, sorption of lead resulted in a 10% decline in lead concentration in their test solution in four hours, while subsequent desorption resulted in a 10% increase in lead concentration after four hours.

Stainless Steel

SS casing materials are often used when conditions warrant a strong, durable, corrosion-resistant material. Of the two types available, Type 316 is somewhat less likely than type 304 to be affected by pitting and corrosion caused by organic acids, sulfuric acid, and sulfur-containing species (Barcelona et al., 1983). However, long exposure to very corrosive conditions may result in chromium and nickel contamination (Barcelona et al., 1983), or iron, manganese, and chromium contamination (U.S. EPA, 1987) of samples. A field study by Barcelona and Helfrich (1986) found that stagnant water samples from SS installations showed higher levels of ferrous iron and lower levels of dissolved sulfide than nearby PTFE and PVC wells, suggesting leaching from the SS and precipitation of sulfide by the excess iron. However, these workers demonstrated that

proper well-purging techniques eliminated this stagnant water from ground-water samples, providing representative ground-water samples.

Laboratory experiments conducted by Parker et al. (1990) examined the potential for sorption on type 304 and 316 SS casing materials. These workers conducted experiments with aqueous solutions of arsenic, cadmium, chromium, and lead at concentrations of 50 µg/L and 100 µg/L and found that after 10 hours, sorption on both type 304 and type 316 caused a 10% decline in arsenic concentration in the test solution. Cadmium concentrations increased 10% in five hours due to leaching from type 304, before returning to initial concentrations after 72 hours. Cadmium leaching from type 316 caused a maximum 30% increase after 20 hours, with concentrations still 20% above initial values after 72 hours. No measurable sorption of chromium occurred for type 304, but 13% losses in 13 hours were observed for type 316. Sorption of lead on type 304 materials led to 20% losses after only four hours of exposure, and approximately 10% for type 316. Parker et al. (1990) concluded from this work that determinations of the concentrations of cadmium, chromium, and lead may be impacted by long-term contact with stainless steel materials. Unfortunately, these workers did not address whether well purging would eliminate these impacts and provide representative ground-water samples.

In a study with five halogenated hydrocarbons, Reynolds et al. (1990) found type 316 SS caused losses of bromoform and hexachloroethane over a five-week period. Losses of these compounds from the test solution were insignificant until one week, after which concentrations dropped up to 70% from initial concentrations of 20 to 45 µg/L. The losses were attributed to reactions involving the metal surfaces or metal ions released from the surfaces and not to sorption (Reynolds et al., 1990). A study by Parker et al. (1990) with ten organic compounds at concentrations of approximately 2 mg/L, found that type 304 and type 316 SS casing resulted in no detectable sorption or leaching effects after six weeks.

Other Metallic Materials

Steel materials other than stainless steel may be more resistant to attack from organic solutions than polymers, but corrosion is a significant problem, particularly in high dissolved-solids, acidic environments (Barcelona et al., 1985a). Ferrous materials may adsorb dissolved chemical constituents or leach ions or corrosion products such as oxides of iron and manganese (Barcelona et al., 1988a). In addition, galvanized steel may contribute zinc and cadmium species to ground-water samples. The weathered steel surfaces, as well as the solid corrosion products themselves, increase the surface area for sorption processes and may therefore act as a source of bias for both organic and inorganic constituents (Barcelona et al., 1985a; Barcelona et al., 1983). Reynolds et al. (1990) determined that galvanized steel showed a 99% reduction in concentrations of five halogenated hydrocarbons in a five-week sampling period. Aluminum casing caused concentration reductions of 90% for four of the compounds. Although many of these aspects of steel materials have not been quantified for typical ground-water environments, they may be a significant source of sample error.

Alternate Materials

Although not as widely tested or used, FRE may represent a rigid well material with relatively low potential for sample bias. In a 72-hour laboratory study, none of the 129 priority pollutants were detected to be leached from a powdered sample of the material (Cowgill, 1988). A three-week dwell-time study of casing materials by the same investigator resulted in detection of no base/neutral or acid compounds. Gillham and O'Hannesin (1990) concluded that sorption of benzene and other aromatic hydrocarbons onto FRE was slightly greater than onto rigid PVC but less than onto PTFE.

Borosilicate glass, another little-used well material, revealed no sorption effects after a 34-day exposure to five halogenated hydrocarbons (Reynolds et al., 1990). Of the ten well materials tested in that study, only the borosilicate glass showed no sorption characteristics. The low potential for sample error indicated by that study suggests that further investigation of borosilicate glass may be warranted to determine its suitability for ground-water sampling.

Flexible Materials

Semi-rigid and flexible materials are used for transfer tubing and other flexible components of the sampling/analysis train. In general, these materials contain plasticizers for flexibility that give them a higher potential than rigid materials to sorb or leach compounds. Latex rubber tubing, flexible PVC, and low density PE were all found to sorb greater quantities than more rigid materials (Reynolds et al., 1990).

In a study of five tubing materials in solutions of four chlorinated hydrocarbons, Barcelona et al. (1985b) found that most sorption occurred in the first 20 minutes of exposure. With the exception of tetrachloroethylene, the materials ranked in order of increasing sorption PTFE, PP, PE, PVC, and silicone. PE showed the highest sorption of tetrachloroethylene. Desorption from all materials occurred rapidly with the same ranking: PTFE desorbed a maximum of 13% of the sorbed concentrations after one hour while silicone desorbed 2%. From the results of this work, Barcelona et al. (1985b) estimated sorptive losses of chlorinated hydrocarbons from sampling tubing under typical flow rates. As an example, using 15 m of 1/2-inch tubing, initial concentrations of 400 µg/L for the four halocarbons, and a sample delivery rate of 100 mL/min, these workers predicted 21, 29, 48, 67, and 74% sorptive losses for PTFE, PP, PE, PVC, and silicone tubing, respectively.

Sorption tests conducted by Barker et al. (1987) found that flexible PTFE led to 17% sorptive losses of benzene and 58% losses of p-xylene after two weeks. For PE, 49% losses of benzene and 91% losses of p-xylene were observed in two weeks. As found in other studies, initial rapid losses were followed by gradual concentration declines in all compounds. Desorption of these compounds followed a similar pattern, approximately 40% of the initial benzene mass and 20% of the initial p-xylene masses desorbed. Laboratory tests conducted by Gillham and O'Hannesin (1990) showed PVC and PE tubing caused sorptive losses of over 10% within five minutes of exposure to six hydrocarbons in solution. After 24 hours, 90% losses for the PVC and 80% losses for the PE had occurred.

These studies suggest that flexible PTFE tubing has lower potential for sorption and leaching than other materials, particularly PVC and silicone. However, even PTFE tubing may have significant impacts on concentrations of organic compounds in ground-water samples, depending on duration of contact. It is clear that the sorption and leaching affects of all materials used as tubing or other flexible portions of the sampling/analysis train should be considered when designing the sampling program. Those materials that demonstrate high potential for sorption and/or leaching should be avoided if those processes could impact concentrations of the compounds of interest to the investigation.

A further source of sample bias with respect to tubing is transmission of compounds or gases through the tubing materials. In a study of PE and PTFE, Barker et al. (1987) detected 2 µg/L benzene and 15 µg/L toluene passing through PE tubing within three days and 15 µg/L and 100 µg/L, respectively, after six days. Subsequent flushing of the tubing with three tubing volumes of clean water reduced the concentrations of both compounds detectable inside the tubing but they were still detectable after twenty volumes were flushed. Under the same conditions, the compounds did not pass through the PTFE tubing in detectable concentrations. These workers suggest that this mechanism may lead to sample bias in other polymeric materials, although perhaps at rates somewhat less than those exhibited by the flexible PE tubing, and could influence conclusions about when well purging procedures or remediation activities are complete. Holm et al. (1988) studied the diffusion of gases through FEP tubing, and found that the amount of gas transferred is proportional to the tubing length and inversely proportional to the flow rate through the tube. Calculations by the authors suggest that, given initially anoxic ground water, oxygen diffusion through sampling tubing could lead to detection of DO and changes in iron speciation within tens of feet. The results of these studies clearly indicate the potential errors that transmission through flexible tubing might introduce when sampling for both organic and inorganic compounds. This source of error can be reduced by using appropriate tubing materials for the sampling conditions and by minimizing tubing lengths.

Selection of Materials

It is clear from laboratory studies of casing materials that concentrations of trace metals and hydrocarbons can be impacted by sorption and leaching from PTFE, PVC, and metallic casing materials. However, laboratory studies do not attempt to duplicate the complicated, interrelated physical, chemical, and biologic conditions present in the field that may cause materials to behave very differently in the hydrogeologic environment. It is also important to keep in mind that most of these experiments were conducted under static conditions and may not adequately represent field conditions where stagnant water is generally replaced with fresh ground water during well purging. In the field, sorption of compounds onto casing materials between sampling events may not affect subsequent ground-water samples, as long as adequate purging andsampling procedures are conducted. Desorption of previously sorbed compounds after long-term exposure may be of somewhat greater importance because continuous desorption may impact trace-level concentrations, which might have important implications to remedial investigations where concentrations are expected to eventually reach non-detectable levels. But again, proper selection and implementation of materials and purging and sampling methods will reduce the impact of these processes.

Given the above discussion and current state of research, some generalizations may be made about the applicability of casing materials to various ground-water contamination scenarios, assuming that reducing sample error is the primary criterion for selection. When monitoring for low hydrocarbon concentrations in non-corrosive ground water, SS and PVC casing may be appropriate choices. Because PTFE has been shown to introduce error into hydrocarbon determinations, it may be most applicable under conditions where SS and PVC are not. As examples, SS would not be appropriate in corrosive ground water or where determination of trace metal concentrations is of primary concern and PVC wells would be inappropriate in situations where solvents in moderate to high concentrations could dissolve the PVC material. A summary of the properties of rigid PVC, PTFE, and SS materials that may introduce sample error is shown in Table 3.

Laboratory studies indicate that the potential for error from flexible tubing is much greater than from rigid materials. For this reason, efforts should be made to use tubing with low potential for sorption and leaching and to minimize tubing length and time of contact. It appears that sample error can be significantly reduced by substituting flexible PTFE for PVC and silicone where possible.

MONITORING WELL PURGING

Purging stagnant water from monitoring wells prior to sampling is considered essential to collection of samples representative of ambient ground water. Stagnant water may result from biological, chemical and physical processes occurring between sampling events. These processes may include biological activity, sorption/desorption reactions with materials of the well, leaching from the materials of the well, degassing and volatilization, atmospheric contamination, and foreign material entering the well from ground surface.

An effective purging method must allow for flushing of the well and sampling device of stagnant water without causing undesirable physical and chemical changes in the adjacent water-bearing zone that may bias subsequent samples. Important aspects of purging include purge volume, pumping rate, depth of the purging device, and purging methods for low-yield wells. Field experiments have shown that purging has important impacts on sample chemistry, perhaps greater than other aspects of sampling protocol such as sampling device and materials (Barcelona and Helfrich, 1986).

Purge Volume

To ensure complete purging of a ground-water monitoring well, there must be established criteria to determine when the water in the well is representative of ambient ground water. Three criteria commonly advocated to determine appropriate purge volume have been described by Gibs and Imbrigiotta (1990) as: (1) a specific, predetermined number of well-bore volumes, (2) stabilization of the values of field chemical indicator parameters (such as temperature, pH, and EC), and (3) hydraulic equilibrium between water stored in the casing and water entering the casing.

TABLE 3. PROPERTIES OF COMMONLY-USED WELL CASING MATERIALS THAT MAY IMPACT GROUND-WATER SAMPLE QUALITY

Material	Properties
Polytetrafluoroethylene (PTFE)	Moderate potential for sorption of hydrocarbons.
	Low potential for leaching of organic constituents.
	Some potential for sorption and leaching of metals, but less than with thermoplastic and metallic materials.
	Particularly resistant to chemical attack, including aggressive acids and organic solvents.
	Not subject to corrosion.
	Resistant to biological attack.
Stainless Steel (SS)	Very low potential for sorption of hydrocarbons.
	Not subject to leaching of organic constituents.
	Significant potential for sorption and leaching of metals.
	Subject to chemical attack by organic acids and sulfur-containing species.
	Subject to corrosion.
	Subject to biological attack.
Polyvinylchloride (PVC)	Potential for sorption of hydrocarbons, but may be less than with fluoropolymers.
	Leaching of organic constituents may occur through chemical degradation by organic solvents.
	Sorption and leaching of some metals.
	Subject to chemical attack by organic solvents.
	Not subject to corrosion.
	Resistant to biological attack.

The use of a specific number of well-bore volumes as the sole criterion for purge volume has been applied extensively in ground-water sampling with recommendations in regulations and the literature ranging from less than one to over 20 (Herzog et al., 1991). In addition, definitions of well-bore volume have included the volume contained within the casing, that volume plus the pore volume of the filter pack, and the volume of the entire borehole. Despite its widespread use, the well-bore volume approach does not directly address the issue of obtaining representative ground water because there is no proven relation between the number of well volumes removed and the completion of purging. The combination of details of well construction, contaminant distribution, and geologic and hydrochemical conditions result in unique conditions at every well such that the volume of water required for purging cannot be determined a priori. It is impossible to predict the magnitude of error that might be introduced by arbitrarily choosing a number of well volumes that results in incomplete purging.

Determining purge volume by measuring field parameters is also widely used. The assumptions implied in this approach are that; (1) as these parameters stabilize, stagnant water in the well has been replaced by ambient ground water, and (2) this water contains representative concentrations of the compounds of interest. However, field experiments conducted by Gibs and Imbrigiotta (1990) showed that field parameters often stabilized before the concentrations of VOCs. In almost 90% of their experiments, field parameter measurements stabilized when three well casing volumes had been purged while VOC concentrations stabilized after three well volumes in only about half of the cases. Likewise, Pearsall and Eckhardt (1987)observed in a series of field experiments that trichloroethylene concentrations continued to change after three hours of pumping at 1.2 L/min while field parameters stabilized within 30 minutes. Furthermore, measurements of individual field parameters may not reach stable values at the same purge volume suggesting that some parameters are more sensitive to purging than others. For example, Pionke and Urban (1987) found that temperature, pH, and EC values of purge water from 14 wells studied generally stabilized before dissolved oxygen and nitrate concentrations. Puls et al. (1990) found that while temperature, pH, and EC values generally stabilized in less than a single well-bore volume, other indicators such as dissolved oxygen and turbidity required up to three well-bore volumes before stabilization. Puls et al. (1990) considered reduction of turbidity to stable values using low pumping rates as critical to the collection of representative metals samples. It should be pointed out that in all of the cases mentioned above, reliance on commonly measured parameters (temperature, pH, and EC) alone would apparently have underestimated the proper purge volume. These results suggest that the choice of purge indicator parameters should be made such that the indicators are sensitive to the purging process and relate to the hydrochemical constituents of interest. This can be accomplished by evaluating the patterns of indicator parameters and ground-water constituents during well purging (a purge-volume test) to determine the appropriate purge volume.

Another implied assumption of the field parameter approach is that purging will result in the stabilization of all constituent concentrations at approximately the same purge volume. In many hydrogeologic systems this assumption may not be valid. For example, in aquifers contaminated by several VOCs, concentration trends during pumping may be very different. In an evaluation of a purge-volume test, Smith et al. (1988) found that concentrations of two compounds started relatively high and decreased with purging to below detectable levels. Two other compounds that were undetected at three casing volumes were detected at four casing volumes and their concentrations increased until stabilizing at ten casing volumes. A fifth compound remained at a constant concentration throughout the purge-volume test. The authors did not report the concentrations observed or the volumes pumped, but it is clear that under these

conditions the choice of purging volume could significantly impact interpretations of contaminant concentrations.

It is important to keep in mind that the distribution of contaminants in limited plumes within a ground-water system is generally in contrast to the more homogeneous distribution of natural hydrochemical conditions in space and time. Consequently, attaining stable concentrations of field parameters, or even gross chemistry, may not indicate a representative sample of the targeted aquifer volume around a monitoring well (Keely and Boateng, 1987). As a result, these workers suggest that the 'inherent variability of the concentration of contaminants in many plumes far outstrip the additional variability potentially induced by incomplete purging,' and recommend that spatial and temporal variations in contaminant concentrations be studied to determine optimum purge volumes.

Methods of determining purge volume by estimating when hydraulic equilibrium occurs between water stored in the casing and water entering the casing may be useful where conservative, non-varying constituents are being monitored. However, determining hydraulic equilibrium by estimating the time at which water levels in the well are no longer affected by casing storage (the method of Papadopulos and Cooper, 1967) may lead to erroneous results (Gibs and Imbrigiotta,1990). These workers compared the calculated hydraulic equilibrium volume to measurements of field parameters and VOC concentrations during several well purging experiments and found that the calculated volume consistently underestimated the volumes required to reach both stable field measurements and stable VOC concentrations. The casing storage method might provide an approximation of purge volume under conditions where conservative, non-varying constituents are being monitored but the available evidence suggests that only sampling for the constituents of interest will provide a direct indication of when their concentrations stabilize.

Recent research reviewed by Puls et al. (1990) demonstrates that contaminants may be transported in ground water by association with colloidal-sized particles which are generally described as particles less than 10 μm in diameter. Where contaminant transport by association with colloids is an important mechanism, obtaining representative concentrations of mobile colloids becomes critical to sample representativeness. However, the acts of purging, sampling, and even placing the sampling device in the well have been demonstrated to significantly impact colloidal suspension in the sampling zones of monitoring wells (Puls et al., 1991; Kearle et al., 1992). If a significant portion of contaminants are transported in association with colloids, the results of these investigations and others suggest minimizing or eliminating purging, minimizing sampling flow rates (100 to 500 mL/min), and using dedicated sampling devices placed within the well intake may all be necessary to collect representative ground water samples. This low-volume approach to purging and sampling was earlier proposed by Robin and Gillham (1987) when sampling for conservative, non-varying parameters in high-yield wells. Using non-reactive tracers, these workers demonstrated that natural ground water movement through the well intake was sufficient to prevent the formation of stagnant water with respect to conservative, non-varying parameters, making purging large volumes unnecessary. Robin and Gillham (1987) pointed out that, under these hydraulic and hydrochemical conditions, representative samples can be collected with little or no purging using dedicated devices positioned within the well intake. In order to resolve the issue of low-volume purging, however, it appears that more research is necessary to better understand colloid movement in ground-water environments, their importance to contaminant transport, and their implications to purging and sampling techniques.

Purge Rate and Depth

It was suggested previously that the pumping rate at which purging is conducted may impact sampling results. Although few detailed studies have been conducted to directly address this issue, the results of a few specific field studies suggest the types of impacts that purging rates might have on sampling results. For example, Imbrigiotta et al. (1988) reported that purging rates of 40 L/min were found to produce VOC concentrations up to 40% higher than concentrations obtained at purging rates of 1 L/min. Likewise, purging with a high-speed submersible pump at a rate of 30 L/min was found to generally produce higher colloid concentrations and larger particle sizes than a low-speed pump at rates lower than 4 L/min (Puls et al., 1990). Despite these colloid differences, however, metals and cation concentrations did not necessarily correlate to pumping rate. Both investigators attributed the variability to the effects that different pumping rates had on the distribution of hydrochemical conditions near the well. Imbrigiotta et al. (1988) further concluded that the variability in VOC concentrations caused by purging rate was of the same magnitude as that observed in a comparison of seven types of sampling devices, suggesting that purging rate may be at least as important to the collection of representative samples as the type of device utilized. Puls et al. (1990) suggested that the colloid differences might also have resulted from entrainment of normally non-mobile suspended particulates in the wells.

Although the issue remains unresolved, it appears that employing pumping rates that allow sample collection with minimal disturbance of the sample and the hydrochemical environment in and near the well may aid in minimizing sampling error. To this end, it has been suggested that the purging rate be chosen such that the rate of ground water entering the well intake is not significantly higher than the ambient ground-water flow rate (Puls and Barcelona, 1989). Under typical hydraulic conditions, this may be possible with pumping rates between 100 and 500 mL/min.

The depth at which purging is conducted may also affect sample representativeness. At high pumping rates or in low- and medium-yield wells, purging at depths far below the air-water interface may introduce error because stagnant water from the well above the pump may be drawn into the pump inlet. Under these conditions, pumping near the air-water interface significantly reduces the time required to remove stagnant water by reducing mixing from above the pump intake (Unwin and Huis,1983; Robin and Gillham, 1987). Keely and Boateng (1987) suggest lowering the pump during purging so as to further reduce the possibility of migration of stagnant water into the intake during sample collection. On the other hand, under high-yield conditions, placing the pump at the well intake and utilizing low pumping rates may serve to isolate the stagnant water in the well bore above the pump thereby providing representative samples with minimal purging (Barcelona et al.,

1985; Robin and Gillham, 1987). Unwin and Maltby (1988) reported that pumping at virtually any depth within a well, including the intake, may lead to contamination of samples by stagnant water from above the pump inlet although their laboratory investigation demonstrated that at a pumping rate of 1 L/min, samples collected within the well intake contained less stagnant water than samples collected above the well intake. Regardless of the depth of the pumping device, if a stagnant water zone develops near the water surface subsequent movement of the pump or placement of a sampling device through this zone may cause contamination of the device by stagnant water.

As suggested above in the discussion of purge volume, certain hydrogeologic conditions and chemical constituents may require that samples be collected with little or no purging using dedicated devices positioned within the well intake. Under these circumstances, it would also be necessary to utilize low purging and sampling rates so as to minimize disturbance of the sample and sampling environment and to prevent migration of stagnant water from the well bore down into the sampler intake.

Purging in Low-Yield Wells

Purging low-yield wells introduces conditions that by definition don't occur in medium- to high-yield wells. These conditions, which tend to have their greatest impact on constituents that are sensitive to pressure changes and/or exposure to construction materials or the atmosphere, often result from dewatering the filter pack and well intake. Dewatering may produce a large hydraulic gradient between the adjacent water-bearing zone and the filter pack as a result of the large drawdown in the well and the low hydraulic conductivity of the formation. One consequence of this condition may be the formation of a seepage face at the borehole wall causing ground water entering the borehole to flow down the borehole wall and fill the dewatered filter pack from the bottom up. Formation of a seepage face increases the surface area of the interface between the liquid phase (ground water) and vapor phase (headspace in the well) available for transfer of solutes. Another consequence of the large hydraulic gradient is the sudden pressure decline from the pressure head in the water-bearing zone to atmospheric pressure in the pumped well. The sudden release of this pressure may cause losses from solution (by degassing or volatilization) of solutes that have combined partial pressures, with that of water, greater than atmospheric. Finally,because water levels recover slowly in low-yield wells, significant changes in the chemical composition of the ground water may occur through sorption, leaching, or volatilization before sufficient volume is available for sample collection.

In a field study of purging and sampling in low-yield wells, Herzog et al. (1988) found that some VOC concentrations increased significantly from pre-purging conditions during the first two hours of water level recovery. For example, chlorobenzene concentrations increased from 25 µg/L before purging to over 125 µg/L at two hours after purging. Concentrations generally did not change significantly after two hours, although some concentrations declined. Although Herzog (1988) provided no explanation for the observed concentration trends, they were likely caused by more representative ground water entering the well and replacing the purged stagnant water. Smith et al. (1988) reported very different results in their field study of a trichloroethylene plume. Concentrations of trichloroethylene declined from 100 µg/L directly after purging to 10 µg/L 24 hours after purging. In a laboratory study, McAlary and Barker (1987) found that if the water level in a simulated well was drawn down below the intake, VOC concentrations during recovery declined 10% in five minutes and 70% in one hour. These changes were attributed to volatilization from the water as it entered and filled the well.

In summary, aspects of well purging important to collection of representative samples include purging volume, pumping rate, depth of the purging device, and time of sampling in low-yield wells. Although error is strictly dependent on individual well and site conditions, the available evidence suggests that order-of-magnitude errors may easily result from improper purging techniques. In low-yield wells, time of sampling is clearly an important source of error although there are too few data available to completely understand concentration trends in these situations.

Contamination concentrations during purging vary in ways that are often difficult to predict, and various compounds may even exhibit opposite trends. To estimate the appropriate purge volume, it may be necessary to conduct preliminary purge-volume tests with sampling at regular intervals during purging. These tests may be useful for determining how indicator parameters and constituent concentrations respond to purging rates, purging volumes, and the distribution of contaminants around the well. In addition, for certain sensitive constituents such as trace metals under certain hydrogeologic and hydrochemical conditions, low-volume purging and sampling should be considered with dedicated sampling devices installed at the well intake.

SAMPLE COLLECTION

Sample collection involves physical removal and transport of ground water from depth (generally from a monitoring well) to ground surface and into a sample container. As such, collection methods may have great potential for alteration of the sample's chemical state. Sampling devices must be chosen and used carefully to ensure that error is minimized. Important aspects of sample collection include sampling device, collection time after purging, and sampling depth.

Chemical Impacts

Sampling devices can cause chemical changes in the sample by contact with materials of the device (sorption, desorption, or leaching) or by the physical action of the device. Although the materials of the device are a potentially significant source of sample error, that topic was discussed previously and the following discussion will address chemical changes produced only by the operation of the sampling device.

Because fluid pressure in the saturated zone is greater than atmospheric, ground-water samples brought to the surface will tend to be under higher pressure conditions than the ambient atmosphere. Exposure of these samples to the lower atmospheric pressure will cause degassing and/or loss of volatile constituents until the partial pressures of the contained volatile components reaches equilibrium with atmospheric pressure. Degassing may cause losses of oxygen (O_2), methane (CH_4), nitrogen (N_2), or carbon dioxide (CO_2), while volatilization might affect any solute that exists as a liquid, solid, or gas under in situ

ground-water temperature and pressure conditions (Gillham et al., 1983). Furthermore, loss of CO_2 may raise the pH which can lead to precipitation of dissolved constituents, particularly iron (Gibb et al., 1981). Constrictions in the flow path within a device may also raise the sample pH by changing the partial pressure of CO_2 (Herzog et al., 1991).

Exposure of samples to the atmosphere, or the driving gas used in some devices, may introduce oxygen causing oxidation of iron, manganese, cadmium, or other species. Oxidation of ferrous iron to ferric iron has important implications to the speciation and concentrations of many constituents in ground water samples (Herzog et al., 1991). Contaminants may also be added to the sample by exposing it to the atmosphere or driving gas.

Sampling Devices

Sampling devices designed for use in conventional monitoring wells can be divided into four general types: grab, positive displacement (no gas contact), suction lift, and gas contact (Pohlmann and Hess, 1988). Grab samplers include open bailers, point-source bailers, and syringe samplers. Positive displacement samplers are usually submersible pumps such as bladder pumps, gear-drive pumps, helical-rotor pumps, and piston pumps. Suction lift devices include peristaltic pumps and surface centrifugal pumps while gas contact pumps include those devices that lift water to the surface by direct gas pressure. Submersible centrifugal pumps, which operate on the principle of positive displacement at low flow rates, develop a partial vacuum at the pump impellers at higher flow rates. For this reason, high-speed submersible centrifugal pumps without variable motor speed capability should be considered as distinct from positive displacement pumps. On the other hand, submersible centrifugal pumps are now available that can be used in 5.1-cm (2-inch) diameter wells and that allow adjustment of the motor speed to produce very low flow rates. If used at low flow rates, these low-speed pumps could conceivably eliminate the application of a partial vacuum to the sample and thereby can be considered as positive displacement pumps. Discussion of the operating principles of many of ground-water sampling devices, and their potential for sample bias, can be found in Gillham et al. (1983).

Sampling devices for conventional monitoring wells can be used either portably or in a dedicated mode. Portable devices are used to collect samples in more than one well and so may cause cross-contamination between installations or sampling events if not properly decontaminated. Dedicated devices are permanently installed in a single well and are generally not removed for cleaning between sampling events. Dedicated samplers, when also used for well purging, may not have adequate flow control for effective purging in large wells (high discharge rate) and sampling (low discharge rate). Furthermore, parts of dedicated samplers may sorb contaminants during periods of contact with ground water between sampling events and then release them during sample collection. Alternatively, if inappropriate materials are used in the construction of dedicated samplers, contaminants may leach from these materials between sampling events.

To study the effects of sampling devices on sample quality, investigations have been conducted both in the laboratory and in the field. Laboratory studies can provide values of absolute sample error by testing under controlled conditions, particularly constituent concentration. However, by their very nature, laboratory experiments represent ideal conditions that can never be duplicated in the field and therefore may not include important field-related errors. On the other hand, field studies include all the physical, chemical, biological, and operating conditions present in field sampling efforts, but the true concentration of the constituents of interest are unknown. As a result, field comparison studies cannot provide values of absolute sample error, only the relative ability of individual devices to recover the constituent of interest.

Values of field chemical indicator parameters can often be the first indication of sample errors due to sampling device. Laboratory investigations of a wide range of sampling devices by Barcelona et al. (1984) revealed that pH and redox potential (Eh) were the most sensitive to sampling device. The largest errors were produced by a peristaltic pump (an increase of 0.05 pH units and a 20 mV decline in Eh). All tested devices had O_2 and CH_4 losses of 1% to 24%, although positive displacement devices and an open-top bailer resulted in the lowest losses and the highest precision in that study. A field study by Schuller et al. (1981) found that, as a result of CO_2 stripping, an air-lift pump and a nitrogen-lift pump produced pH values up to 1.0 pH unit higher than a peristaltic pump and opentop bailer. Other field studies concluded that open-top and dual-valve bailers produced no more error in field parameter values than bladder pumps (Houghton and Berger, 1984). In that study, which used bladder pump values as a standard for comparison, a peristaltic pump and a high-speed submersible centrifugal pump had increases in pH of about 0.06 pH units and approximately 20% declines in dissolved oxygen (DO) concentrations. A gas-driven piston pump had an increase in DO of 8% to 36%. Temperatures increased up to 5% in samples collected with the peristaltic and piston pumps and 14% in samples collected with the high-speed submersible centrifugal pump.

Most major dissolved ions are relatively stable and not greatly affected by collection method. Schuller et al. (1981) determined that concentrations of calcium, chloride, fluoride, potassium, magnesium, and sodium collected at two field sites were not significantly affected by the choice of suction, gas-contact, or bailer device. Dissolved metals, on the other hand, are very sensitive to sample aeration and degassing during sampling. Schuller et al. (1981) found that iron and zinc concentrations in samples collected with two gas contact devices were, at most, 30% of those collected with either a peristaltic pump or a bailer. Field studies of 18 wells with seven sampling devices by Houghton and Berger (1984) showed significant declines in metals concentrations for a gas contact device when compared to positive displacement pumps, grab samplers, and a peristaltic pump. Houghton and Berger (1984) also found that coprecipitation of arsenic and zinc with iron led to significant losses of these constituents in samples collected with a high-speed submersible centrifugal pump.

Sampling device impact on VOC concentrations is of particular importance because of the high sensitivity of these compounds to sample aeration and degassing and the critical need for accurate VOC data in many site investigations. Several laboratory experiments have shown that positive displacement devices (bladder, piston, and helical-rotor pumps) and conven-

tional grab samplers (open-top and dual-valve bailers) provide the most accurate VOC concentrations (Barcelona et al. 1984; Unwin, 1984; Schalla et al., 1988; Unwin and Maltby, 1988). Although the bladder pump and bailers that Barcelona et al. (1984) tested produced less than 3% losses in VOC concentrations, these same devices produced up to 10% losses in other studies, even under carefully-controlled conditions. Suction and gas-contact devices tested in these studies, and a study of peristaltic pumps by Ho (1983), resulted in 4% to 30% losses in VOC concentrations. Of those devices that performed well, no relation was found between sampler accuracy and VOC concentration over a range of 80 to 8000 µg/L (Barcelona et al., 1984; Unwin, 1984). The devices that performed poorly, however, often revealed significant increases in error as concentration increased (Barcelona et al., 1984). From these laboratory studies it appears that certain classes of samplers, specifically suction and gas-contact, can lead to significant error in VOC concentrations as a result of volatilization from the sample during collection.

A positive relation between increased losses of VOCs from solution with increase in Henry's law constant was predicted by Pankow (1986) based on theoretical considerations of the factors leading to bubble formation in water during sampling. Physical experiments have shown a strong positive correlation between compound volatility and Henry's law constant for a peristaltic pump, some correlation for a helical-rotor pump, but no correlation for a bailer and bladder pump (Unwin and Maltby, 1988). On the other hand, Barker et al. (1987) found no clear correlation for a peristaltic pump and gas-drive sampler and Barker and Dickhout (1988) found no clear correlation for a peristaltic, bladder, or inertial-lift pump, although the range of Henry's law constants was small. These findings suggest that compound volatility may not be an important source of bias for some positive displacement and grab samplers but there may be potential for losses for samplers that impose a suction on the sample.

Many field comparisons of sampler effectiveness verify the findings of laboratory experiments, despite the increased number of variables involved in the field studies. Investigations involving a variety of field conditions by Muska et al. (1986), Pearsall and Eckhardt (1987), Imbrigiotta et al. (1988), Liikala et al. (1988), Yeskis et al. (1988), and Pohlmann et al. (1990) concluded that positive displacement devices produced the highest VOC concentrations, and therefore introduced the least error into VOC determinations. The accuracy of grab samplers was more variable: some studies showed little difference between the VOC recoveries of bailers and positive displacement pumps (Muska et al. (1986), Imbrigiotta et al. (1986), Liikala et al. (1988)), but Imbrigiotta et al. (1987), Yeskis et al. (1988), and Pohlmann et al. (1990) reported that bailer VOC concentrations were significantly lower than positive displacement pumps; 46% to 84% lower in the work of Yeskis et al. (1988). Pearsall and Eckhardt (1987) found that a bailer was as accurate as a positive displacement pump at concentrations in the range of 76 to 79 µg/L but recovered 12% to 15% lower concentrations in the range 23 to 29 µg/L.

Another grab sampler, the syringe sampler, also produced mixed results. Muska et al. (1986) concluded that syringe sampler accuracy and precision were not significantly different from those of the positive displacement pumps while Imbrigiotta et al. (1988) concluded that syringe sampler accuracy was lower than the pumps but that precision was comparable. Other samplers field-tested produced significant error: a peristaltic pump and surface centrifugal pump were found by Pearsall and Eckhardt (1987) to be less accurate, but not necessarily less precise than the other samplers tested. Imbrigiotta et al. (1988) found the same for a peristaltic pump.

In ground-water environments charged with dissolved gases, collection of accurate VOC samples can be even more problematic. VOC losses of 9% to 33% were produced by a peristaltic pump in laboratory and field studies of water containing high CO_2 (laboratory study) and CH_4 (field study) concentrations (Barker and Dickhout, 1988). Losses of 13% to 20% were produced by a bladder pump in the laboratory study, while an inertial-lift pump produced no losses. No differences between results from these two pumps were observed in the field. The CO_2 concentrations used in the laboratory investigation were higher than under environmental conditions, but this study nonetheless suggests that degassing during sample collection, even with a positive displacement pump, can lead to significant error in VOC concentrations (Barker and Dickhout, 1988).

Several "in situ" devices have been developed to alleviate some of the problems inherent to conventional monitoring wells and sampling devices. These devices generally utilize sample containers under reduced pressure to collect samples directly from the water-bearing zone, without exposure to the atmosphere or excessive agitation. In a field study, Pohlmann et al. (1990) found that two types of in situ devices delivered samples with VOC concentrations that were not significantly different from those collected by a bladder pump in a conventional monitoring well.

Although the field studies outlined above cannot provide values of absolute sample error, they do provide information on the effectiveness of various devices under actual operating conditions. The results of the laboratory studies, in conjunction with field studies, indicate that suction pumps are very likely to introduce significant error into VOC determinations. Grabsamplers, especially bailers, are also likely to produce errors if not operated with great care because their successful operation is closely related to operator skill. Under certain conditions, for certain parameters, and if operated by skilled personnel, bailers can produce representative samples. However, much of the research outlined here indicates that positive displacement pumps consistently provide the lowest potential for sample error. Appropriate application of most types of positive displacement pumps can reduce sampling device contribution to error well below the levels of some other aspects of ground-water sampling protocol.

A summary of the impacts that some commonly-used sampling devices have on ground-water sample quality is shown in Table 4 which was compiled from the sources referenced in this section and Nielsen and Yeates (1985).

Collection Depth and Time after Purging

The length of time between well purging and sample collection may influence the representativeness of samples by exposing ground water to the effects of atmospheric diffusion, interaction with well materials, and contaminant volatilization. Smith et al.

TABLE 4. SOME IMPACTS THAT THE OPERATING PRINCIPLES OF GROUND-WATER SAMPLING DEVICES MAY HAVE ON GROUND-WATER SAMPLE QUALITY (WITH THE EXCEPTION OF GRAB SAMPLERS, IT IS ASSUMED THAT THESE DEVICES REMAIN IN THE WELL DURING THE SAMPLING PROCESS).

Operating Principle	Impacts
Gas Contact	Contact with drive gas may cause loss of dissolved gases and increase pH.
	Contact with drive gas may volatilize sensitive solutes.
	Exposure to driving gas may introduce contaminants or oxidize sensitive constituents.
Grab	Contact with atmosphere during sample recovery and transfer may cause loss of dissolved gases and increase pH.
	Contact with atmosphere during sample recovery and transfer may volatilize sensitive solutes.
	Exposure to atmosphere during sample recovery and transfer may introduce contaminants or oxidize sensitive constituents.
	May be contaminated when passing through zone of stagnant water.
Positive Displacement	Minimal if discharge rate is low.
Suction Lift	Application of suction to sample may cause loss of dissolved gases and increase pH.
	Application of suction to sample may volatilize sensitive solutes.
High-Speed Submersible Centrifugal	Suction applied at pump intake may cause loss of dissolved gases and increase pH.
	Suction applied at pump intake may cause volatilization of sensitive solutes.
	Application of excessive head to the sample may cause degassing or volatilization.
	Heat produced by pump motor may increase sample temperature.

(1988) found that trichloroethane concentrations in a well declined from 170 µg/L immediately after purging to 10 µg/L 24 hours later. To ensure consistency and to reduce potential errors when sampling in high-yield wells, it is generally recommended that samples be collected immediately following completion of well bore purging. In low-yield wells, however, low water level recovery rates may require that sampling be delayed until sufficient volume is available. Determination of sample collection time in low-yield wells is more problematic and may require site-specific sampling experiments.

To reduce potential errors caused by mixing with stagnant well water during sampling, research has suggested that the sampler intake be located either within the screened interval (Giddings, 1983; Bryden et al., 1986; Robin and Gillham, 1987) or at the top of the screened interval (Unwin, 1982; Barcelona and Helfrich, 1986) so samples can be obtained soon after fresh ground water enters the well bore. However, in cases where wells are screened over a long interval, it is important to determine if contaminants are vertically stratified in the well. Pearsall and Eckhardt (1987) found that TCE concentrations of samples collected at the top of a 10-foot screened interval were 30% lower than those collected at the bottom and attributed the difference to vertical stratification of VOCs within the screened interval. Errors associated with sampler intake placement have not been quantified to date but are likely strongly controlled by conditions at each well.

The use of samplers that must pass through the zone of stagnant water that invariably remains near the water level, even in a properly-purged well, may also introduce error. For example, grab samplers, which often require repeated entry and retrieval from the well during sampling, may be contaminated by this zone of stagnant water or may mix stagnant water into the water column. Likewise, if the purging device is not used for sampling, removal of the purging device and installation of the sampling device may have a similar effect. The use of a dedicated device for both purging and sampling would significantly reduce this source of error but may introduce others.

SAMPLE FILTRATION

Ground-water samples collected for analysis of certain constituents are often filtered in the field prior to transfer to the appropriate container. Reasons for filtration include prevention of geochemical reactions that might occur with particulates during sample shipment and storage, removal of suspended sediments so as to analyze only dissolved constituents, and removal of fine-grained sediments which might interfere with laboratory analyses. Because filtration may contribute to sample error by the method employed or by the choice to filter, it is of the utmost importance to confirm the objectives of the sampling program and the implications of filtering when choosing whether to filter and, if so, the filtration technique.

Puls and Barcelona (1989) point out that if mobile trace metal species are of interest to the investigation filtration may remove metals adsorbed onto some colloidal particles, leading to underestimates of dissolved metals concentrations and, therefore, concentrations of mobile species. Conversely, if the objective of metals analysis is to quantify total dissolved metals concentrations, colloids with sorbed metals that pass through the filter material may result in overestimates of dissolved metals concentrations (Puls and Barcelona, 1989). These workers indicate that filtration should not be used as a means of removing from the sample particulates that result from poor well construction, purging, or sampling procedures because the misapplication of filtration may introduce substantial bias to trace metal determinations. If filtration is deemed necessary, it should be conducted soon after sample collection as temperature changes, CO_2

invasion, or the presence of particulates may have adverse effects on trace metal concentrations or dissolved solids content (Unwin, 1982). Factors important to proper field filtration include filter pore size, material, and method, and holding time prior to filtration.

Filter pore size has very important implications for determinations of metal species and major ions in ground-water samples as a result of the inclusion of undissolved material. Constituents showing the greatest sensitivity to filter pore size include iron and zinc (Gibb et al., 1981), iron and aluminum (Wagemann and Brunskill, 1975), and iron, aluminum, manganese, and titanium (Kennedy et al., 1974). In all cases, larger filter pore sizes produced higher concentrations of these constituents because the larger pore-size filters allowed more particulates to pass. In fact, Kennedy et al. (1974) found that concentrations of some metal species in samples filtered through 0.45 µm filters were up to five times higher than in samples filtered through 0.10 µm filters. These results suggest that if field-filtering is deemed necessary, smaller pore size filters may reduce sample error.

Sorptive losses of trace metals during filtration can also introduce error into metals determinations. Truitt and Weber (1979) found that both cellulose acetate and polycarbonate 0.4 µm filter membranes sorbed copper and lead from solution. For example, losses of copper averaged 8.6% with cellulose acetate membranes and 1.1% with polycarbonate membranes. Gardner and Hunt (1981) found that sorption of lead onto cellulose acetate membranes resulted in losses of 20 to 44% from a synthetic solution. These losses were reduced to 5 to 24% by pre-rinsing the filter apparatus with the test solution (Gardner and Hunt, 1981). Studies by Jay (1985) found that virtually all filters require pre-rinsing to avoid sample contamination by leaching of anions from the filter material.

Although filter material and pore size have been the subject of considerable research, less effort has been directed toward understanding the effects of filtration method on dissolved constituents. Of the few studies available, Stolzenburg and Nichols (1985) investigated the effects of sampling and filtration method on concentrations of iron and arsenic. Their laboratory study showed that samples that were vacuum-filtered after a 10-minute holding time delay experienced iron losses of 20% to 90% and arsenic losses of 45% to 100% compared to in-line filtered samples. The ranges of percentages were due to the use of several types of sampling devices. Later experiments by Stolzenburg and Nichols (1986) added immediate vacuum filtering of samples. Both immediate and delayed vacuum-filtration produced similar iron concentrations but these concentrations were 17% to 67% lower than concentrations produced by in-line filtration. In both the 1985 and 1986 reports, in-line filtering produced concentrations that were comparable to the source concentrations of approximately 8 mg/L iron and 0.05 mg/L arsenic suggesting that in-line filtration methods were the most effective of those tested. These experiments also suggested that filtration method may cause greater losses of certain constituents than the type of sampling device used. Unfortunately, commonly-used pressure filtration methods were not compared to in-line and vacuum filtration methods in these experiments.

Clearly, sample filtration can lead to substantial error in trace metal determinations even if procedures are carefully followed. Because of this great potential for error, filtration should not be used to correct for sedimentation problems that result from poorly designed or constructed wells or incomplete development. If filtration is deemed necessary, pre-cleaning the filters can reduce error. In addition, the limited research into filtration methods in ground-water investigations suggests that in-line methods may result in the least sample error. However, even under ideal conditions, sample filtration may lead to significant error in determinations of metals concentrations, suggesting that analysis of both filtered and non-filtered samples should be considered.

EQUIPMENT DECONTAMINATION

Contaminants on equipment that contacts ground water and samples, including drilling equipment, well materials, sampling devices, and sample bottles may be another source of sample error. Error may be introduced by the addition of contaminants to ground water or samples (contamination) or by the conveyance of ground water and/or contaminants from one sampling installation or zone to another (cross-contamination). Cross-contamination is most often a problem when equipment, particularly sampling devices, is used portably but not properly cleaned between installations. The process of cleaning equipment before installation or after sampling is generally referred to as decontamination.

Drilling equipment can be a source of gasoline, diesel fuel, hydraulic fluid, lubricating oils and greases, and paint, all of which can be introduced into the subsurface during drilling operations. In addition, contaminated soil, scale, or water from the site may enter the borehole directly or by adhering to drilling pipe or other down-hole equipment. If these contaminants originate from other sites or boreholes, cross-contamination may result (Fetter, 1983). Steam cleaning is often recommended as a method of decontaminating the drilling rig and equipment before use and between boreholes. In addition, placing down-hole drilling equipment on plastic sheeting or other appropriate material while not in use may reduce contamination from soils or other sources of contaminants at ground surface.

Well casing and screen materials may contain residues of the manufacturing process including cutting oils, cleaning solvents, lubricants, and waxes (Aller et al., 1989). These residues must be removed prior to well installation to prevent contamination or other chemical impacts on samples. A procedure generally recommended is to wash the casing in a strong detergent solution followed by a tap water rinse (Barcelona et al., 1983; Curran and Tomson, 1983) although steam cleaning or a high-pressure hot water wash may be required for removal of some oils, lubricants, and solvents (Aller et al., 1989).

Equipment used portably can lead to cross-contamination by transferring water and contaminants from one installation to another. In a survey of state and federal environmental regulatory agencies, Mickham et al. (1989) found that procedures for decontamination of sampling equipment generally include a tap water rinse, acid or solvent rinse (depending on type of contamination), organic-free water rinse, and air drying. The survey also showed that equipment that does not directly contact samples is generally cleaned by detergent washes and steam cleaning. These workers found little research into the effectiveness of decontamination procedures.

Korte and Kearl (1985) suggest that high-volume pumping may sufficiently clean sampling pumps. In contrast, field experiments conducted by Matteoli and Noonan (1987) determined that 90 minutes of pumping clean water through 200 feet of PTFE tubing was required to reduce the concentrations of several organic and inorganic constituents to below detection levels. These workers found that the time required for effective decontamination was generally related to the type of constituent. Freon was still detectable after 120 minutes of pumping.

The effects of cross-contamination can be reduced or eliminated by utilizing equipment dedicated to individual monitoring wells. As discussed previously, a potential disadvantage of this approach may be interactions between the device and ground water in the well between sampling events.

The use of plastic sample bottles may be another potential source of contamination through leaching of organic and inorganic constituents from the bottle materials (Gillham et al., 1983). An experiment comparing acid-washed and water-washed plastic sample containers determined that the risk of contamination from trace elements in the bottles was greatest for cadmium, copper, and zinc (Ross, 1986). In some cases copper concentrations were 50 times higher in samples collected in bottles that were not acid-washed. Moody and Lindstrom (1977) suggested that plastic sample containers are most effectively cleaned with rinses in both hydrochloric acid and nitric acid to leach impurities from the plastics. Their study further determined that, after acid-washing, PTFE and PE containers were the least contaminating plastic or polymeric materials.

Interference of ground-water sample chemistry may result from direct introduction of foreign materials to ground water and samples or from crosscontamination. Although it appears that currently used decontamination procedures are adequate in a general way, little research has been conducted to determine the effectiveness of specific procedures for individual contaminants. Because they are not standardized, the contribution to sample error of a particular procedure must be evaluated, perhaps on a case-by-case basis.

To prevent crosscontamination when using sampling devices portably, rinsate blanks (also referred to as equipment blanks) should be collected to ensure the effectiveness of decontamination procedures. This may be accomplished by flushing or filling the device with Type II reagentgrade water and collecting a sample of the rinsate water. Analysis of rinsate blanks for the contaminants being sampled will provide an indication of the effectiveness of the cleaning method (U.S. EPA, 1986) and indicate if modifications of the procedures are required.

SAMPLE TRANSPORT AND STORAGE

Ground-water samples require proper containers, treatment, transport, and storage to ensure the chemical and physical state of the sample is preserved until analysis. Factors that could potentially lead to error include volatilization, adsorption, diffusion, precipitation, photodegradation, biodegradation, and cross-contamination (Parr et al., 1988). Methods developed, and widely accepted, to minimize these effects are summarized in U.S. EPA (1986) and Herzog et al. (1991).

To reduce the potential for bias during sample handling, appropriate chemical preservation of samples should take place immediately upon collection. Increases in pH of 0.3 to 0.4 units and declines in iron and zinc concentrations of several orders of magnitude have been observed within seven hours of sample collection (Schuller et al., 1981). These investigators also noted slight declines in the concentrations of calcium, potassium, magnesium, manganese, and sodium in unpreserved samples within 48 hours of collection. To ensure immediate preservation, it may be advisable in some cases to add chemical preservatives to bottles immediately before sample collection. If this method is utilized it is important to prevent the bottle from overflowing which might cause the loss of some of the preservative.

Plastic bottles are usually used for metals and major ions samples to avoid the sorption effects that may occur with glass. Most types of plastic bottles can be cleaned with hydrochloric acid and nitric acid rinses which effectively leach impurities from the material. PTFE and PE bottles tend to not leach impurities to samples (Moody and Lindstrom, 1977) and therefore are the easiest to clean and have the lowest potential to contaminate samples. The quantities of impurities leached in these studies are in the very low ng/cm^2 range, generally below the levels in most site investigations. Sorption of metals onto plastic bottles, although normally not a problem, is reduced by acidifying the sample and thereby keeping the metals ions in solution (Parr et al., 1988). Clearly, if adequate cleaning is carried out and pre-analysis holding times are not exceeded, contamination of major ion and trace metal samples by sample bottles is unlikely.

Organic samples are usually placed in glass containers to avoid the chemical interferences that may occur with plastic bottles. The borosilicate glass used in bottles for water samples for organic analyses is easily cleaned and has very little potential for contamination of samples or sorption from samples.

Cross-contamination of VOC samples during transport and storage can be minimized if accepted procedures are carefully followed. The evidence presently available indicates that cross-contamination of VOC samples at concentrations typical of hazardous waste sites is negligible under conditions normally present during sample storage (Levine et al., 1983; Maskarinec and Moody, 1988). Levine et al. (1983) did note, however, the thickness of the PTFE lining under the VOC vial septum was critical to the prevention of cross-contamination and that contamination was evident when samples were stored near vials containing saturated aqueous solutions of VOCs. Trip blanks can be utilized to evaluate the potential for contamination of samples during shipment to the laboratory. These blanks, which consist of reagent-grade water in bottles of the same type used for sampling, can be shipped to the site and laboratory in the same shipping containers used for samples.

The length of time that a sample can be stored without degradation is related to the potential sources of error covered here. If adequate measures are taken to reduce these errors, chemical alteration of the sample during storage can be minimized. Using commonly-accepted storage methods, concentrations of VOCs have been shown to be stable after 34 days (Friedman et al., 1986) and 56 days (Maskarinec and Moody, 1988).

ANALYTICAL TECHNIQUES

To gain perspective into the relative magnitude and importance of errors introduced during ground-water sampling, it is useful to quantify the errors involved in laboratory analysis. Potential sources of error in the laboratory include glassware, reagents, laboratory preparation techniques, and analytical equipment and apparatus (Lewis, 1988). It is beyond the scope of this document to discuss how each of these aspects of laboratory operation can impact sample quality except to say that errors can be detected and controlled by the use of various quality-control checks. Vitale et al., (1991) describe the blanks, duplicate samples, and spikes that ensure the identification of laboratory error. Through the use of these checks, analytical errors often can be quantified, unlike many aspects of sampling protocol where comparison to 'true' concentrations is usually impossible.

In a review of the EPA Contract Laboratory Program (CLP) database for gas chromatograph/mass spectrometer (GC/MS) analysis of VOCs, Flotard et al. (1986) analyzed the deviations in reported concentrations from actual concentrations in blind performance evaluation samples. These deviations can be considered measures of analytical errors, with underreported concentrations considered negative error and overreported concentrations considered positive error. The Flotard et al. (1986) study found errors in reported concentrations of 22 VOCs from -46.4% for 1,1-dichloroethane to +6.5% for bromoform. The results for methylene chloride exhibited an apparent error of +36.6% but this value was attributed to laboratory contamination of samples and not analysis error. Their review indicated that 55% of the 22 evaluated VOCs resulted in reported concentrations that were more than 20% lower than actual concentrations. Interlaboratory errors from 35 laboratories were found to be from -3.9% to zero, although data from only three compounds were analyzed.

A similar review of the CLP database for semi-volatile analyses conducted by Wolff et al. (1986) concluded that the greatest analytical errors were associated with phenolic compounds, whose concentrations were consistently underreported. Other classes of semi-volatiles showed no general trends. In that study, analytical errors ranged from -48% for 1,3-dichlorobenzene and 2,6-dinitrotoluene to +12% for 4-chlorophenylphenylether. The review indicated that 60% of the 33 compounds evaluated showed analytical errors in excess of -20%, slightly more than for VOC analyses. Interlaboratory errors for six compounds ranged from -51% for phenol-d_5 to -16% for p-terphenyl, considerably greater than for the volatile analyses.

The CLP database has also been evaluated for errors introduced by inorganic analytical methods (Aleckson et al., 1986). These workers found that analytical errors ranged from -26.5% to +10.0%, with most errors falling in the range -10.0% to zero. The greatest negative errors were found for selenium, silver, and thallium.

Barcelona et al. (1989) tabulated laboratory errors for inorganic constituents during an intensive time-series investigation of ground-water chemistry variation. They found that errors in determinations of major ions in external performance samples ranged from -8.1% (potassium) to +12.1% (total iron). An evaluation of eight analytical laboratories was conducted by Rice et al. (1988) as part of a uranium mill tailings ground-water quality investigation. Constituents of interest included total dissolved solids, major ions, trace metals, and radionuclides. Analysis of external performance samples during the study showed that 67% of all analyses were within the acceptable range but that 60% of the reported values were higher than the known concentrations. Iron and aluminum were among the constituents showing the highest analytical errors.

SUMMARY AND CONCLUSIONS

As shown here, many aspects of ground-water investigations may introduce error into determinations of concentrations of hydrochemical constituents. The potential errors associated with many of these aspects are summarized in Table 5.

Errors produced during certain aspects of sampling programs can be identified, quantified, and controlled through the use of accepted procedures in conjunction with performance evaluation samples. For example, equipment decontamination and sample transport and storage have considerable potential for introducing sample error if not conducted in a careful and consistent manner. In the case of equipment decontamination, collection and analysis of rinsate blanks from cleaned equipment can be useful for evaluating the effectiveness of decontamination procedures. Likewise, errors that may occur during sample transport can be identified by the use of trip blanks that are transported to the site and laboratory in the same shipping containers as field samples. An aspect that may require particular attention and further research is the effectiveness of decontamination of flexible tubing used for conveying samples from the sampler to sample bottle.

The potential errors associated with other aspects of sampling programs are relatively well understood and can be minimized through appropriate choice of equipment and materials. For instance, advances in sampling device design and construction have resulted in the development and widespread use of positive displacement sampling devices whose operation generally introduces little sample error. For most compounds, including VOCs, positive displacement devices allow collection of accurate and precise samples, with concentrations of VOCs typically within 10% of true concentrations. Some grab samplers, particularly bailers, may also produce representative samples but their effectiveness is highly dependent on mode of operation and the constituents of interest. Under unfavorable field conditions or when operated improperly, bailers may produce errors in VOC concentrations from -10% to -80% or more. Most other types of samplers produce errors of unpredictable magnitude but show VOC errors of at least -20% in controlled laboratory experiments. The unpredictable magnitude of errors associated with many of these devices also means that they often cannot provide the precise, or repeatable, measurements usually associated with positive displacement devices. As a result, the use of positive displacement sampling devices may minimize the introduction of error into determinations of the concentrations of sensitive hydrochemical constituents. Use of other types of devices may introduce error of unpredictable magnitude.

Potential impacts of materials used in well and sampler construction have been demonstrated, but the implications of these effects in a field setting remain unclear. Laboratory comparison studies conducted under static conditions have demonstrated

the potential for rigid PTFE, PVC, and metallic materials to introduce error into concentrations of some trace metals and hydrocarbon compounds. However, little work has been conducted under conditions simulating dynamic ground- or sample-water flow or, more importantly, well-purging effects. Despite these unresolved issues, materials' impacts can be minimized by choosing well materials compatible with the objectives of the sampling program and the hydrogeologic and hydrochemical conditions of the site. The proper choice of materials can reduce chemical effects on water stored in the well between sampling events and make removal of stagnant water during well purging less difficult. When monitoring for low hydrocarbon concentrations in non-corrosive ground water, SS and PVC casing may be the most appropriate choices. Because PTFE has been shown to introduce error into hydrocarbon determinations, it may be most applicable under conditions where SS and PVC are not considered appropriate. For example, SS would probably not be considered an appropriate material in corrosive ground water or where determinations of trace metal concentrations are of primary concern. Likewise, PVC probably would not be considered an appropriate material in situations where solvents in moderate to high concentrations might dissolve the PVC material.

Flexible tubing can introduce significant error through sorption of contaminants onto tubing material, leaching of constituents of the tubing material into sampled water, and possibly transmission of organic compounds and gases through tubing walls. These errors are generally greater than for rigid materials and may be particularly important during site remediation efforts when declines in ground-water concentrations may be masked by desorption of previously sorbed compounds. Laboratory research has demonstrated the potential for errors under static conditions, but further research is required to understand how sorption/desorption mechanisms can impact samples during the dynamic sampling process. These studies suggest, however, that sample error can be minimized by substituting PTFE for other types of flexible materials.

Filtration of samples for trace metals determinations may introduce sample error either by the equipment and methods utilized or by the actual decision to filter. Due to the presence of colloidal sized particles in ground water, filtration can have dramatic impacts on determinations of the concentrations of both mobile and total dissolved metals. Indiscriminate filtration of metals samples may lead to gross errors in these concentrations and result in erroneous conclusions about ground-water transport of metals. In view of this, the objectives of the sampling program must be carefully considered before samples are filtered. If it is decided to filter samples, in-line filtration with pre-cleaned, lower pore-size filters can reduce errors associated with filtration.

In contrast to most aspects of the sampling process, errors introduced during laboratory analysis may be relatively well quantified. Analysis of the CLP database has shown errors in reported concentrations of performance samples of -20% to -30% for volatile and semivolatile compounds and -10% to zero for inorganic constituents. Errors in analytical methods, as with sample transport, sample storage, and equipment decontamination, can be quantified for individual investigations by analyzing standards and blind quality evaluation samples. Although the magnitude of analytical error may be greater than the error introduced during some aspects of sample collection, analysis of quality evaluation samples leads to easier identification and quantification of analytical error.

Errors associated with other aspects of site investigations, including well drilling and construction, are more difficult to identify because true concentrations of hydrochemical constituents are unknown in field investigations. During the drilling phase of site investigations, hydrogeologic disturbances can be minimized by utilizing appropriate drilling methods. Likewise, drilling-related hydrochemical disturbances can be reduced by avoiding the use of fluids that might alter ground-water chemistry through ion exchange reactions or exposure to organic polymers. Well construction and development methods appropriate to the site hydrogeologic conditions are capable of removing artifacts from the drilling process and improving the hydraulic efficiency of the well with minimal impact on subsequent samples. Proper design, installation, and isolation of cement or bentonite seals reduces the potential for chemical alterations from these materials. Any of these aspects of drilling and well construction can lead to large errors if not carefully controlled, however, the magnitude of error is directly related to site conditions and the extent to which methods have been misapplied. Careful consideration and application of methods and materials during well drilling and construction can significantly reduce sample error.

Well purging method, purging rate, and the volume purged prior to sample collection all possess great potential for introducing significant error when sampling for sensitive constituents. For example, setting the purging device far below the air-water interface and using a high purge rate may contaminate samples by allowing stagnant water to mix with sampled water. However, it is possible to identify these potential sources of error and modify purging procedures to minimize the errors. Conducting a preliminary purge test may aid in identification of the depth and rate that results in the most representative samples, however, determination of when purging is complete (purge volume) may be more difficult. Although purge volume can be calculated by several indirect methods, this volume may not directly correlate with the volume of water required to provide representative samples. In particular, stabilization of the values of field chemical indicator parameters such as temperature, pH, and EC may not coincide with stabilization of other hydrochemical parameters and constituents. Due to the often complex three-dimensional distribution of many contaminants, concentrations of individual constituents may not stabilize at the same time, or may never stabilize. Despite these possibilities, the potential for sample error can be reduced by choosing indicator parameters that are sensitive to the purging process and relate to the constituents of interest.

To reduce error when sampling for constituents that may be associated with colloids, or other very sensitive constituents, it is particularly important to minimize disturbance of the samples and the sampling environment during the purging and sampling process. To this end, reducing or eliminating purging, minimizing purging and sampling flow rates, and using dedicated sampling devices placed within the well intake interval should all be considered. Because this issue remains unresolved, general recommendations are not possible and it may be necessary to conduct preliminary purge tests to determine how indicator

parameters and concentrations of important constituents vary with purging rate, volume, method, and distribution of contaminants around the well. Inadequate determination of these factors may lead to order-of-magnitude, or more, errors in concentration determinations, especially in low-yield wells.

The errors most critical to sampling programs are those that are difficult or impossible to identify because important conclusions may be unknowingly based on erroneous or inadequate data. Well location and design are aspects of sampling that are very likely to produce undetected errors. Errors produced by well location are virtually impossible to identify because their magnitude is entirely specific to that particular location. The appropriate placement of a well can mean the difference between detection of a contaminant plume or missing it entirely, so the potential for error is virtually infinite. Even if a well is located in the targeted zone of contamination or plume, little can be deduced about small-scale hydrogeologic properties or contaminant distribution without a well-designed monitoring network that accounts for individual site characteristics and program objectives.

Well design, particularly the depth and interval of the well intake, can also be a large potential source of undetectable errors. To delineate the vertical distribution of contaminants at a single location, samples must be collected at specific depths, hence, wells must be screened over short intervals and adequately sealed between sampling zones. Dilution and cross-contamination resulting from long-screened wells or poor well seals may produce order-of-magnitude errors in concentrations that far outweigh errors produced in all other aspects of the sampling process. For example, dilution of samples collected from long-screened remediation wells may mask true contaminant concentrations, leading to erroneous conclusions about the effectiveness of remedial efforts.

In conclusion, it can be stated that virtually all aspects of ground-water investigations, from well location to laboratory analysis, have the potential to introduce error into the determinations of concentrations of hydrochemical constituents. General definition of the magnitude of potential errors is difficult because errors will be influenced by the complex interaction of geologic, hydraulic, and hydrochemical conditions unique to each site, as well as the design and performance of the sampling program. Potential sources of error related to site conditions must be identified during early phases of the remedial investigation (RI) and then minimized by careful design of the sampling program. Modifications to the program design may then be necessary to address issues that might arise as the RI proceeds. Methods of detecting errors that may be introduced during the performance of the sampling program must be utilized so that these errors can be identified and minimized. However, errors that are difficult or impossible to detect may provide the greatest obstacles to the collection of representative data.

TABLE 5. POTENTIAL SOURCES OF ERROR ASSOCIATED WITH ELEMENTS OF GROUND-WATER SAMPLING PROGRAMS AT HAZARDOUS WASTE SITES.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Well Intake Length	Long-screened and multi-screened wells may lead to cross-contamination or contamination dilution.	Easy to Moderate	Identify specific zones of interest. Use intake length appropriate to program objectives and hydrogeologic and hydrochemical conditions.	Difficult	Compare with data from short-screen wells or field-screening methods.
Well Intake Depth	Well intake may miss zone of interest.	Easy to Moderate	Identify specific zones of interest. Use intake length appropriate to program objectives and hydrogeologic and hydrochemical conditions.	Difficult	Compare with data from other wells or field-screening methods.
Well Intake Design	Presence of particulates in samples.	Easy to Moderate	Design in conjunction with filter pack for hydrogeologic conditions.	Easy to Moderate	Turbid samples.
Filter Pack	Presence of particulates in samples. Reaction with filter pack materials or introduced contaminants may alter hydrochemistry. Vertical connection of naturally isolated zones if filter pack too long. Invasion of borehole seal materials if filter pack too short.	Easy to Moderate	Design in conjunction with well intake for hydrogeologic conditions. Use clean, non-reactive materials. Install with tremie pipe and measure depths and volumes during installation to ensure correct placement.	Easy to Moderate	Turbid samples. Sorption/leaching studies of materials before installation.

(Continued)

TABLE 5. CONTINUED.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Borehole Seals	If improperly placed, bentonite materials may alter hydrochemistry through ion exchange. If improperly placed, cement may elevate values of ground-water pH, EC, alkalinity, calcium concentration.	Moderate	Design for hydrogeologic conditions. Isolate seals from sampling zone. Install with tremie pipe and measure depths and volumes during installation to ensure correct placement.	Moderate to Difficult	Bentonite: High sodium concentrations if sodium bentonite used and samples are highly contaminated. Cement: Sample pH over 10, and high EC, alkalinity, and calcium concentrations.
Well Location	Inadequate coverage of area of investigation.	Moderate	Careful design of monitoring well network.	Difficult	Compare with data from nearby wells or field-screening methods.
Drilling	Depends on method. Contamination by drilling or other fluids may alter hydrochemistry. Smearing and mixing of fluids and sediments at borehole wall. Cross contamination within borehole.	Moderate	Careful consideration and application of methods that are appropriate for program objectives and hydrogeologic and hydrochemical conditions. Minimize use of water-based drilling fluids and additives. If constituents sensitive to atmospheric exposure will be sampled, minimize use of air-based drilling fluids. Determine the chemical quality of drilling fluids used. Use appropriate development methods to minimize impacts of drilling.	Moderate to Difficult	Drilling fluid contamination: Depends on composition of fluid. Compare with data from nearby wells and field-screening methods. Evaluate chemical quality of fluids used.
Well Development	Depends on method. Incomplete development may lead to turbid samples or poor hydraulic efficiency. Alteration of hydrochemistry by development action. Introduction of contaminants (including air and water).	Easy to Moderate	Careful consideration and application of methods that are appropriate for program objectives and hydrogeologic and hydrochemical conditions. Avoid adding fluids to well. If adding fluids is necessary, determine the chemical quality of the fluids used.	Moderate	Turbid samples and production of sediments during pumping may indicate incomplete development or inadequate design of filter pack and well intake. If fluids were added, evaluate chemical quality of fluids used.
Materials	Depends on material, contaminants, hydrochemical conditions, and time of contact. Sorption/desorption of chemical constituents. Leaching of constituents from materials' matrix. Biologic activity. Possible transmission through flexible materials.	Easy to Moderate	Select materials that are appropriate for program objectives and hydrogeologic and hydrochemical conditions. Use appropriate well purging techniques.	Difficult	Sorption/leaching studies of materials before installation. Detection after installation depends on material, contaminants, hydrochemical conditions, and time of contact.

(Continued)

TABLE 5. CONTINUED.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Well Purging	Incomplete removal of stagnant water (water affected by contact with atmosphere and well and sampling device materials). Disturbance of ambient hydrochemical conditions.	Easy to Moderate (Moderate to Difficult under low-yield conditions)	Choose indicator parameters that are sensitive to purging process and relate to the chemical constituents of interest. Conduct purge-volume test to determine when parameters or constituents of interest reach stable values. Determine if low flow-rate and/or low volume purging is appropriate. If not, minimize volume of stagnant water above device intake by purging near water surface or lower device during purging or before sampling. Avoid drawing water level below top of well intake.	Easy to Moderate (Moderate to Difficult under low-yield conditions)	Conduct purge-volume test to determine when parameters or constituents of interest reach stable values
Sampling Device	Depends on operating principle of sampling device. Sorption, desorption, and leaching from materials. Degassing or volatilization from sample. Atmospheric contamination.	Easy	Select device that is appropriate for sample type, hydrochemical conditions, and program objectives.	Moderate to Difficult	Depends on sampler type. Compare with data collected with other devices.
Sample Collection Time and Depth	Mixing with stagnant water in well. As time after purging increases, water in well becomes more stagnant.	Easy	Collect samples from within or immediately above well intake. Use appropriate sampling rate. Avoid moving sampler within water column during sampling. High-yield wells: Sample immediately after purging. Low-yield wells: Determine appropriate time based on response of well and purge-volume test.	Moderate to Difficult	Test different scenarios and compare results, although may be very difficult to determine which results are the most representative.
Sample Filtration	Type of filter system used and length of pre-filtration holding time determines extent of temperature changes, atmospheric contamination, degassing, and sorption onto particulates. Filter pore size may affect passage of certain constituents and suspended material. Filter material and filter pre-cleaning may affect results. Erroneous conclusions about metals concentrations may result from association of metals with colloids.	Easy to Moderate	Determine of filtration is necessary for the objectives of the program. Minimize pre-filtration holding time. Use pre-cleaned in-line filters. Some situations may warrant use of pore sizes other than 0.45µm.	Moderate	Compare analytical results of filtered and unfiltered samples. Compare analytical results of different filtration methods.

(Continued)

TABLE 5. CONTINUED.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Equipment Decontamination	Cross-contamination between wells if sampling equipment is used portably. Incomplete removal of residues from manufacture or contaminants from storage, transport, or use.	Easy	Use appropriate cleaning and decontamination procedures.	Easy	Collect rinsate blanks after cleaning.
Sample Preservation	Changes in hydrochemistry during sample shipment and storage.	Easy	Use appropriate physical and chemical preservation procedures.	Moderate to difficult.	Indirectly identified by evaluating how well procedures are being followed.
Sample Transport and Storage	Cross-contamination between sample bottles. Materials' effects from sample bottles. Loss of volatile constituents.	Easy	Use appropriate sample bottle type and cleaning procedure. Do not exceed sample holding times.	Easy	Transport trip blanks with samples.
Laboratory Analysis	Deviation from true concentrations.	Moderate	Use appropriate analytical methods and laboratory procedures.	Easy to Moderate	Analyze blind performance evaluation samples, blanks, and standards.

REFERENCES

Aleckson, K. A., J. W. Fowler, and Y. Joyce Lee, 1986. Inorganic analytical methods performance and quality control considerations. In: *Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Fifth Volume*, ASTM STP 925, C. L. Perket, ed. American Society for Testing and Materials. pp. 112-123.

Aller, L., T. W. Bennett, G. Hackett, R. J. Petty, J. H. Lehr, H. Sedoris, D. M. Nielsen, and J. E. Denne, 1989. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. U.S. Environmental Protection Agency. EPA/600/4-89/034. 221 p.

Andricevic, R. and E. Foufoula-Georgiou, 1991. A transfer function approach to sampling network design for groundwater contamination. *Water Resources Research.* Vol. 27, No. 10. pp. 2759-2769.

Barcelona, M. J., J. P. Gibb, and R. A. Miller, 1983. A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling. Illinois State Water Survey Contract Report No. 327. U.S. Environmental Protection Agency. EPA/600/52-84/024. 78 p.

Barcelona, M. J., 1984. TOC determinations in ground water. *Ground Water.* Vol. 22, No. 1. pp. 18-24.

Barcelona, M. J., J. A. Helfrich, E. E. Garske, and J. P. Gibb, 1984. A laboratory evaluation of ground water sampling mechanisms. *Ground Water Monitoring Review.* Vol. 4, No. 2. pp. 32-41.

Barcelona, M. J., J. P. Gibb, J. A. Helfrich, and E. E. Garske, 1985a. Practical Guide for Ground-Water Sampling. Illinois State Water Survey Contract Report No. 374. 94 p.

Barcelona, M. J., J. A. Helfrich, and E. E. Garske, 1985b. Sampling tubing effects on groundwater samples. *Analytical Chemistry.* Vol. 57, No. 2. pp. 460-464.

Barcelona, M. J. and J. A. Helfrich, 1986. Well construction and purging effects on groundwater samples. *Environ. Sci. Technol.* Vol. 20, No. 11. pp. 1179-1184.

Barcelona, M. J., J. A. Helfrich, and E. E. Garske, 1988a. Verification of sampling methods and selection of materials for groundwater contamination studies. In: *Ground-Water Contamination: Field Methods, Special Technical Publication 963,* A. I. Johnson, ed. American Society for Testing and Materials. pp. 221-231.

Barcelona, M. J., G. K. George, and M. R. Schock, 1988b. Comparison of Water Samples from PTFE, PVC, and SS Monitoring Wells. U.S. Environmental Protection Agency. EPA/600/X-88/091. 37 p.

Barcelona, M. J., H. A. Wehrmann, M. R. Schock, M. E. Sievers, and J. R. Karny, 1989. Sampling Frequency for Ground-Water Quality Monitoring. U.S. Environmental Protection Agency. EPA/600/4-89/032. 191 p.

Barker, J. F., G. C. Patrick, L. Lemon, and G. M. Travis, 1987. Some biases in sampling multilevel piezometers for volatile organics. *Ground Water Monitoring Review.* Vol. 7, No. 2. pp. 48-54.

Barker, J. F. and R. Dickhout, 1988. An evaluation of some systems for sampling gas-charged ground water for volatile organic analysis. *Ground Water Monitoring Review.* Vol. 8, No. 4. pp. 112-120.

Berens, A. R., 1985. Prediction of organic chemical permeation through PVC pipe. *Journal of the American Water Works Association.* Vol. 77, No. 1. pp. 57-64.

Boethner, E. A., G. L. Ball, Z. Hollingsworth, and R. Aquino, 1981. Organic and Organotin Compounds Leached from PVC and CPVC Pipe. U.S. Environmental Protection Agency. EPA/600/1-81/062. 102 p.

Brobst, R. B. and P. M. Buszka, 1986. The effect of three drilling fluids on groundwater sample chemistry. *Ground Water Monitoring Review.* Vol. 6. No. 1. pp. 62-70.

Bryden, G. W., W. R. Mabey, and K. M. Robine, 1986. Sampling for toxic contaminants in ground water. *Ground Water Monitoring Review.* Vol. 6, No. 2. pp. 67-72.

Cohen, R. M. and R. R. Rabold, 1987. Numerical evaluation of monitoring well design. In: *Proceedings of First National Outdoor Action Conference,* National Water Well Association, Dublin, Ohio. pp. 267-283.

Cowgill, U. M., 1988. Sampling waters: The impact of sampling variability on planning and confidence levels. In: *Principles of Environmental Sampling,* L. H. Keith, ed. American Chemical Society Professional Reference Book. pp. 171-189.

Curran, C. M. and M. B. Tomson, 1983. Leaching of trace organics into water from five common plastics. *Ground Water Monitoring Review.* Vol. 3, No. 3. pp. 68-71

Driscoll, F. G., 1986. Ground Water and Wells, 2nd Ed. Johnson Division. St. Paul, Minnesota. 1108 p.

Fetter, C. W., 1983. Potential sources of contamination in ground-water monitoring. *Ground Water Monitoring Review.* Vol. 3, No. 2. pp. 60-64.

Flotard, R. D., M. T. Homsher, J. S. Wolff, and J. M. Moore, 1986. Volatile organic analytical methods performance and quality control considerations. In: *Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Fifth Volume,* ASTM STP 925, C. L. Perket, ed. American Society for Testing and Materials. pp. 185-197.

Friedman, L. C., L. J. Schroder, and M. G. Brooks, 1986. Recovery of several volatile organic compounds from simulated water samples: Effect of transport and storage. *Environ. Sci. Technol.* Vol. 20, No. 8. pp. 826-829.

Gardner, M. J. and D. T. Hunt, 1981. Adsorption of trace metals during filtration of potable water samples with particular reference to the determination of filterable lead concentrations. *Analyst.* Vol. 106. pp. 471-474.

Gibb, J. P., R. M. Schuller, and R. A. Griffin, 1981. Procedures for the Collection of Representative Water Quality Data from Monitoring Wells. Cooperative Groundwater Report #7, State of Illinois, Department of Energy and Natural Resources, Champaign, Illinois. 61 p.

Gibs, J. and T. E. Imbrigiotta, 1990. Wellpurging criteria for sampling purgeable organic compounds. *Ground Water.* Vol. 28, No. 1. pp. 68-78.

Giddings, T., 1983. Bore-volume purging to improve monitoring well performance: an often mandated myth. In: *Proceedings of the Third National Symposium on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Columbus, Ohio. pp. 253-256.

Giddings, T., 1986. Screen length selection for use in detection monitoring well networks. In: *Proceedings of Sixth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Dublin, Ohio. pp. 316-319.

Gillham, R. W., M. J. L. Robin, J. F. Barker, and J. A. Cherry, 1983. Groundwater Monitoring and Sample Bias. API Publication No. 4367, American Petroleum Institute. 206 p.

Gillham, R. W. and S. F. O'Hannesin, 1990. Sorption of aromatic hydrocarbons by materials used in construction of ground-water sampling wells. In: *Ground Water and Vadose Zone Monitoring.* D. M. Nielsen and A.I. Johnson, eds. ASTM STP 1053, American Society for Testing and Materials, Philadelphia, Pennsylvania. pp. 108-122.

Herzog, B. L., S. J. Chou, J. R. Valkenburg, and R. A. Griffin, 1988. Changes in volatile organic chemical concentrations after purging slowly recovering wells. *Ground Water Monitoring Review.* Vol. 8, No. 4. pp. 93-99.

Herzog, B., J. Pennino, and G. Nielsen, 1991. Ground-water sampling. In: Practical Handbook of Ground-Water Monitoring. D. M. Nielsen, ed. Lewis Publishers. Chelsea, Michigan. pp. 449-499.

Ho, J. S., 1983. Effect of sampling variables on recovery of volatile organics in water. *Journal of the American Water Works Association.* Vol. 12. pp. 583-586.

Holm, T. R., G. K. George, and M. J. Barcelona, 1988. Oxygen transfer through flexible tubing and its effects on ground water sampling results. *Ground Water Monitoring Review.* Vol. 8, No. 3. pp. 83-89.

Houghton, R. L. and M. E. Berger, 1984. Effects of well-casing composition and sampling method on apparent quality of ground water. In: *Proceedings of The Fourth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Dublin, Ohio. pp. 203-213.

Imbrigiotta, T. E., J. Gibs, J. F. Pankow, and M. E. Rosen, 1987. Field comparison of downhole and surface sampling devices for purgeable organic compounds in ground water. Abstract in: *U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceedings of the Third Technical Meeting, Pensacola, Florida.* B. J. Franks, ed. U.S. Geological Survey. Open-File Report 87-109. pp. E5-E6.

Imbrigiotta, T. E., J. Gibs, T. V. Fusillo, G. R. Kish, and J. J. Hochreiter, 1988. Field evaluation of seven sampling devices for purgeable organic compounds in ground-water. In: *Ground-Water Contamination: Field Methods.* A. I. Johnson, ed. Special Technical Publication 963, American Society for Testing and Materials. pp. 258-273.

Jay, P. C., 1985. Anion contamination of environmental water samples introduced by filter media. *Analytical Chemistry.* Vol. 57, No. 3. pp. 780-782.

Kaleris, V., 1989. Inflow into monitoring wells with long screens. In: *Contaminant Transport in Groundwater.* H. E. Kobust and W. Kinzelbach, eds. A. A. Balkema, Rotterdam. pp. 41-50.

Kearl, P. M., N. E. Korte, and T. A. Cronk. 1992. Suggested modifications to ground water sampling procedures based on observations from the colloidal boroscope. *Ground Water Monitoring Review.* Vol. 12, No. 2. pp. 155-161.

Keely, J. F. and K. Boateng, 1987. Monitoring well installation, purging, and sampling techniques - part 1: conceptualizations. *Ground Water.* Vol. 25, No. 4. pp. 427-439.

Keith, S. J., L. G. Wilson, H. R. Fitch, and D. M. Esposito, 1983. Sources of spatial-temporal variability in ground-water quality data and methods of control. *Ground Water Monitoring Review.* Vol. 3, No. 2. pp. 21-32.

Kennedy, V. C., G. W. Zellweger, and B. F. Jones, 1974. Filter pore-size effects on the analysis of Al, Fe, Mn and Ti in water. *Water Resources Research.* Vol. 10, No. 4. pp. 785-790.

Korte, N. and P. Kearl, 1985. Procedures for the Collection and Preservation of Groundwater and Surface Water Samples and for the Installation of Monitoring Wells. GJ/TMC-08, U.S. Department of Energy. 68 p.

Kraemer, C. A., J. A. Shultz, and J. W. Ashley, 1991. Monitoring well post-installation considerations. In: Practical Handbook of Ground-Water Monitoring. D. M. Nielsen, ed. Lewis Publishers. Chelsea, Michigan. pp. 333-365.

Levine, S. P., M. A. Puskar, P. O. Dymerski, B. J. Warner, and C. S. Friedman, 1983. Cross-contamination of water samples taken for analysis of purgeable organic compounds. *Environ. Sci. Technol.* Vol. 17, No. 2. pp. 125-127.

Lewis, D. L., 1988. Assessing and controlling sample contamination. In: *Principles of Environmental Sampling,* L. H. Keith, ed. American Chemical Society Professional Reference Book.

Liikala, T. L., D. S. Daly, and A. P. Toste, 1988. An Evaluation of the Effects of Well Construction Materials and Groundwater Sampling Equipment on Concentrations of Volatile Organic Compounds. PNL-6585 UC-11. Pacific Northwest Laboratory. 25 p.

Maskarinec, M. P. and R. L. Moody, 1988. Storage and preservation of environmental samples. In: *Principles of Environmental Sampling,* L. H. Keith, ed. American Chemical Society Professional Reference Book. pp. 145-155.

Matteoli, R. J. and J. M. Noonan, 1987. Decontamination of rubber hose and teflon tubing for ground sampling. In: *Proceedings from First National Outdoor Action Conference,* National Water Well Association, Dublin, Ohio. pp. 159-183.

McAlary, T. A. and J. F. Barker, 1987. Volatilization losses of organics during ground water sampling from low permeability materials. *Ground Water Monitoring Review.* Vol. 7, No. 4. pp. 63-68.

McIlvride, W. A. and R. B. Rector, 1988. Comparison of short- and long-screen monitoring wells in alluvial sediments. In: *Proceedings of Second National Outdoor Action Conference,* National Water Well Association, Dublin, Ohio. pp. 277-287.

McIlvride, W. A. and R. B. Weiss, 1988. Drilling method effects on well performance. In: *Proceedings from Second National Outdoor Action Conference,* National Water Well Association, Dublin, Ohio. pp. 277-287.

Meyer, P. D. and E. D. Brill, Jr., 1988. A method for locating wells in a groundwater monitoring network under conditions of uncertainty. *Water Resources Research.* Vol. 24, No. 8. pp. 1277-1282.

Mickham, J. T., R. Bellandi, and E. C. Tiff, 1989. Equipment contamination procedures for ground water and vadose zone monitoring programs: Status and prospects. *Ground Water Monitoring Review.* Vol. 19, No. 2. pp. 100-121.

Miller, G. D., 1982, Uptake and release of lead, chromium, and trace level volatile organics exposed to synthetic well casings. In: *Proceedings of the Second National Symposium on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Dublin, Ohio. pp. 236-245.

Moody, J. R. and R. M. Lindstrom, 1977. Selection and Cleaning of Plastic Containers for Storage. *Analytical Chemistry.* Vol. 49, No. 14. pp. 2264-2267.

Morin, R. H., D. R. LeBlanc, W. E. Teasdale, 1988. A statistical evaluation of formation disturbance produced by well-casing installation methods. *Ground Water.* Vol. 26, No. 2. pp. 207-217.

Muska, C. F., W. P. Colven, V. D. Jones, J. T. Scoglin, B. B. Looney, and V. Price, Jr., 1986. Field evaluation of ground water sampling devices for volatile organic compounds. In: *Proceedings of the Sixth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Dublin, Ohio. p. 235-246.

Nielsen, D. M. and G. L. Yeates, 1985. A comparison of sampling mechanisms available for smalldiameter ground water monitoring wells. *Ground Water Monitoring Review.* Vol. 5. No. 2. pp. 83-99.

Nielsen, D. M. and R. Schalla, 1991. Design and installation of ground-water monitoring wells. In: Practical Handbook of Ground-Water Monitoring. D. M. Nielsen, ed. Lewis Publishers. Chelsea, Michigan. pp. 239-331.

Pankow, J. F., 1986. Magnitude of artifacts caused by bubbles and headspace in the determination of volatile organic compounds in chemistry. *Analytical Chemistry.* Vol. 58. pp. 1822-1826.

Papadopulos, I. S. and H. H. Cooper, Jr., 1967. Drawdown in a well of large diameter. *Water Resources Research.* Vol. 3. pp. 241-244.

Parker, L. V., A. D. Hewitt, and T. F. Jenkins, 1990. Influence of casing materials on trace-level chemicals in well water. *Ground Water Monitoring Review.* Vol. 10, No. 2. pp. 146-156.

Parr, J., M. Bollinger, O. Callaway, and K. Carlberg, 1988. Preservation techniques for organic and inorganic compounds in water samples. In: *Principles of Environmental Sampling,* L. H. Keith, ed. American Chemical Society Professional Reference Book. pp. 221-230.

Paul, D. G., C. D. Palmer, and D. S. Cherkauer, 1988. The effect of construction, installation, and development on the turbidity of water in monitoring wells in fine-grained glacial till. *Ground Water Monitoring Review.* Vol. 8, No. 1. pp. 73-82.

Pearsall, K. A. and A. V. Eckhardt, 1987. Effects of selected sampling equipment and procedures on the concentrations of trichlorethylene and related compounds in ground water samples. *Ground Water Monitoring Review.* Vol. 7, No. 2. pp. 64-73.

Pionke, H. B. and J. B. Urban, 1987. Sampling the chemistry of shallow aquifer systems - a case study. *Ground Water Monitoring Review.* Vol. 7, No. 2. pp. 79-88.

Pohlmann, K. F. and J. W. Hess, 1988. Generalized Ground Water Sampling Device Matrix. *Ground Water Monitoring Review.* Vol. 8, No. 4.

Pohlmann, K. F., R. P. Blegen, and J. W. Hess, 1990. Field Comparison of Ground-Water Sampling Devices for Hazardous Waste Sites: An Evaluation Using Volatile Organic Compounds. U.S. Environmental Protection Agency. EPA/600/4-90/028. 102 p.

Puls, R. W. and M. J. Barcelona, 1989. Ground Water Sampling for Metals Analyses. U.S. Environmental Protection Agency. Superfund Issue Paper. EPA/540/4-89/001. 6 p.

Puls, R. W., J. H. Eychaner, and R. M. Powell, 1990. Colloidal-Facilitated Transport of Inorganic Contaminants in Ground Water: Part I. Sampling Considerations. U.S. Environmental Protection Agency. Environmental Research Brief. EPA/600/M-90/023. 12 p.

Puls, R. W., R. M. Powell, D. A. Clark, and C. J. Paul, 1991. Facilitated Transport of Inorganic Contaminants in Ground Water: Part II. Colloidal Transport. U.S. Environmental Protection Agency. Environmental Research Brief. EPA/600/M-91/040. 12 p.

Reilly, T. E., O. L. Franke, and G. D. Bennett, 1989. Bias in groundwater samples caused by wellbore flow. *Journal of Hydraulic Engineering.* Vol. 115, No. 2. pp. 270-277.

Reynolds, G. W., J. T. Hoff, and R. W. Gillham, 1990. Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ. Sci. Technol.* Vol. 24, No. 1. pp. 135-142.

Rice, G., J. Brinkman, and D. Muller, 1988. Reliability of chemical analyses of water samples - the experience of the UMTRA project. *Ground Water Monitoring Review.* Vol. 8, No. 3. pp. 71-75.

Robin, M. J. L. and R. W. Gillham, 1987. Field evaluation of well purging procedures. *Ground Water Monitoring Review.* Vol. 7, No. 4. pp. 85-93.

Ross, H. B., 1986. The importance of reducing sample contamination in routine monitoring of trace metals in atmospheric precipitation. *Atmospheric Environment.* Vol. 20, No. 2. pp. 401-405.

Scalf, M. R., J. F. McNabb, W. J. Dunlap, and R. L. Crosby, 1981. Manual of Ground-Water Quality Sampling Procedures. National Water Well Association, Dublin, Ohio. 93 p.

Schalla, R., D. A. Myers, M. A. Simmons, J. M. Thomas, and A. P. Toste, 1988. The sensitivity of four monitoring well sampling systems to low concentrations of three volatile organics. *Ground Water Monitoring Review.* Vol. 8, No. 3. pp. 90-96.

Scheibe, T. D. and D. P. Lettenmaier, 1989. Risk-based selection of monitoring wells for assessing agricultural chemical contamination of ground water. *Ground Water Monitoring Review.* Vol. 9, No. 4. pp. 98-108.

Schuller, R. M., J. P. Gibb, and R. A. Griffin, 1981. Recommended sampling procedures for monitoring wells. *Ground Water Monitoring Review.* Vol. 1, No. 1. pp. 42-46.

Smith, R. L., R. W. Harvey, J. H. Duff, and D. R. LeBlanc, 1987. Importance of close-interval vertical sampling in delineating chemical and microbiological gradients in ground water Ssudies. In: *Toxic Waste-Ground-Water Contamination Program Third Technical Meeting,* OFR87-109, U.S. Geological Survey. pp. 33-35.

Smith, F., S. Kulkarni, L. E. Myers, and M. J. Messner, 1988. Evaluating and presenting quality assurance sampling data. In: *Principles of Environmental Sampling,* L. H. Keith, ed. American Chemical Society Professional Reference Book.

Sosebee, J. B., P. C. Geiszler, D. L. Winegardner, and C. R. Fisher, 1982. Contamination of groundwater samples with poly (vinyl chloride) adhesives and poly (vinyl chloride) primer from monitoring wells. In: *Hazardous and Industrial Solid Waste Testing: Second Symposium, January 28-29, 1982,* R. A. Conway and W. P. Gulledge, eds. ASTM Technical Publication 805. pp. 38-50.

Spruill, T. B. and L. Candela, 1990. Two approaches to design of monitoring networks. *Ground Water.* Vol. 28, No. 3. pp. 430-442.

Stolzenburg, T. R. and D. G. Nichols, 1985. Preliminary Results on Chemical Changes in Groundwater Samples Due to Sampling Devices. EPRI EA-4118, Electric Power Research Institute. 84 p.

Stolzenburg, T. R. and D. G. Nichols, 1986. Effects of filtration method and sampling devices on inorganic chemistry of sampled well water. In: *Proceedings of the Sixth National Symposium and Exposition on Aquifer Restoration and Ground-Water Monitoring,* National Water Well Association, Dublin, Ohio. pp. 216-234.

Sykes, A. L., R. A. McAllister, and J. B. Homolya, 1986. Sorption of organics by monitoring well construction materials. *Ground Water Monitoring Review.* Vol. 6, No. 4. pp. 44-47.

Truitt, R. E. and J. H. Weber, 1979. Trace metal ion filtration losses at pH 5 and 7. *Analytical Chemistry.* Vol. 51, No. 12. pp. 2057-2059.

Unwin, J. P., 1982. A Guide to Ground-Water Sampling. Stream Improvement Technical Bulletin No. 362. National Council of the Paper Industry for Air and Stream Improvement, Inc. 124 p.

Unwin, J. P. and D. Huis, 1983. A laboratory investigation of the purging behavior of small-diameter monitoring wells. In: *Proceedings of the Third National Symposium on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Columbus, Ohio. pp. 257-262.

Unwin, J. P, 1984. Sampling ground water for volatile organic compounds: The effects of sampling method, compound volatility and concentration. In: *Proceedings of the Fourth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring,* National Water Well Association, Dublin, Ohio. pp. 214-220.

Unwin, J. P. and V. Maltby, 1988. Investigations of techniques for purging ground-water monitoring wells and sampling ground water for volatile organic compounds. In: *Ground-Water Contamination: Field Methods, Special Technical Publication 963,* A. I. Johnson, ed. American Society for Testing and Materials. pp. 240-252.

U.S. EPA, 1986. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document. OSWER-9950.1, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 208 p.

U.S. EPA, 1987. Handbook: Groundwater. EPA/625/6-87/016. 212 p.

Vitale, R. J., O. Braids, and R. Schuller, 1991. Ground-water sample analysis. In: Practical Handbook of Ground-Water Monitoring. D. M. Nielsen, ed. Lewis Publishers. Chelsea, Michigan. pp. 501-539.

Wagemann, R. and G. J. Brunskill, 1975. The effect of filter pore size on analytical concentrations of some trace elements in filtrates of natural water. *International Journal of Environmental Analytical Chemistry.* Vol. 4, No. 1. pp. 75-84.

Wolff, J. S., M. T. Homsher, R. D. Flotard, and J. G. Pearson, 1986. Semi-volatile organic analytical methods performance and quality control considerations. In: *Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Fifth Volume*, ASTM STP 925, C.L. Perket, ed. American Society for Testing and Materials. pp. 157-171.

Yeskis, D., K. Chiu, S. Meyers, J. Weiss, and T. Bloom, 1988. A field study of various sampling devices and their effects on volatile organic contaminants. In: *Proceedings of Second National Outdoor Action Conference*, National Water Well Association, Dublin, Ohio. pp. 471-479.